CHEMISTRY OF 2-ETHYNYLBIPHENYL-2'-DIAZO METHANE: SYNTHESIS OF DIBENZOBICYCLO[4.1.0]HEPTATRIENE, INTERMEDIATE IN THE AROMATIC CARBENE-ARYL CARBENE REARRANGEMENT

by

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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Abstract of Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of The Requirements for the Degree of Doctor of Philosophy

CHEMISTRY OF 2-ETHYNYLBIPHENYL-2'-DIAZO METHANE: SYNTHESIS OF DIBENZOBICYCLO[4.1.0]HEPTATRIENE, INTERMEDIATE IN THE AROMATIC CARBENE-ARYL CARBENE REARRANGEMENT

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John Peter Mykytka

August, 1974

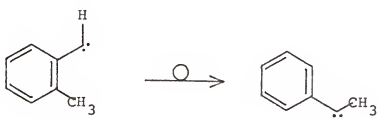
Chairman: W. M. Jones
Major Department: Chemistry

A convenient synthesis of 2-ethynylbiphenyl-2'-carboxaldehyde tosylhydrazone sodium salt is reported. Dibenzobicyclo[4.1.0]heptatriene is formed from photolysis of the salt in dimethyl ether at -110°C, presumably through formation of 2-ethynylbiphenyl-2'-diazo methane which intramolecularly adds to the triple bond. The bicycloheptatriene is trapped with 1,3-butadiene in a Diels Alder reaction and it is the latter adduct which is actually isolated. The carbene-carbene rearrangement of dibenzocycloheptatrieylidene to 9-phenanthrylcarbene can be halted presumably at the same dibenzobicyclopheptatriene intermediate by a sufficient decrease in temperature. The biphenyl diazo methane also undergoes an intramolecular 2 + 3 cycloaddition with the triple bond yielding 3H-phenanthro[9,10-c]pyrazole (a pyrazolenine) which tautomerizes to 2H-phenanthro[9,10-c]pyrazole and also presumably undergoes a second photolysis giving rise to 9-phenanthrylcarbene. The 3H-pyrazole was shown not

to be a precursor of the bicycloheptatriene. The reaction of 9-phenanthrylcarbene and dimethyl ether gives 9-methoxymethyl phenanthrene, which represents loss of methylene between the two reacting species. Apparatus is described which is capable of solution photochemistry from +30°C to -120°C. 2-(Phenylethynyl)-biphenyl-2'-carboxaldehyde tosylhydrazone sodium salt was studied also.

INTRODUCTION

Since the initial definitive report by Joines, Turner and Jones[1] (and the earlier observation by Vander Stouw and Shechter[2]) that an aryl carbene could undergo a rearrangement to another carbene before it reacted in normal carbene fashion, much work has been done in attempting to elucidate the mechanism by which said rearrangement such as (1)→(2) does occur.

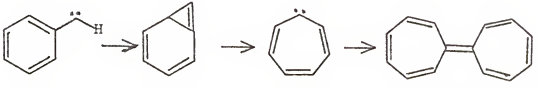


1 2

Within the realm of carbocyclic carbenes, the only prior example of an aryl or aromatic carbene rearrangement (there have been other previous carbene interconversions[3]) was suggested by Cais et al.[4] in the deprotonation of ferrocenyltropylium fluoroborate to give products derived from ring contraction of ferrocenylcycloheptatrienylidene to ferrocenylphenylcarbene, but no mechanism was implied.

Briefly, Joines, Turner, and Jones[1] reported that phenylcarbene (3), generated thermally in the gas

phase, underwent rearrangement presumably through the reactive intermediate (or transition state) (4) to cycloheptatrienylidene (5) which dimerized to heptafulvalene (6). This was supported soon afterward by



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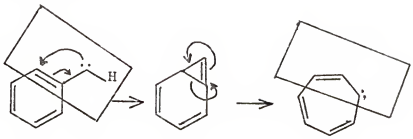
reports from Wentrup and Wilczek,[5] Hedaya,[6,7] M. Jones, Jr.,[8] a complete discussion by Shechter[9] on his earlier work,[2] and further work by Jones.[10] The bicycloheptatriene (4) was proposed, of course, from analogy with the well-known reaction of vinyl carbene to give cyclopropene.[11]

If the vinyl carbene moity in (3) is isolated as diagramed in (7), the fused cyclopropene is formed by attack of the carbene on the double bond as shown (the movement of electrons not implying any orbital considerations). Ring opening of the cyclopropene then proceeds by the reverse mechanism and if the other single bond is broken, the ring expanded carbene (5) is generated, the carbene carbon, of course, being the quatenary or

vinyl bridgehead carbon of (4).



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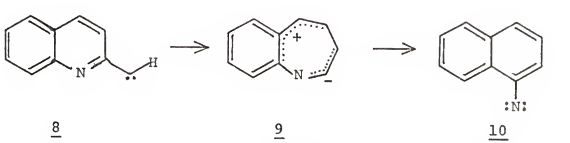
The only other mechanism that has been seriously considered for this interconversion has been an adaptation of the Wolff rearrangement. Its popularity has mainly been enjoyed in nitrene-carbene rearrangements such as quinolylcarbene (8) to 1-naphthylnitrene[12] (10) or the interconversion of labeled 9-phenanthridylnitrene[13] (11)→(13).



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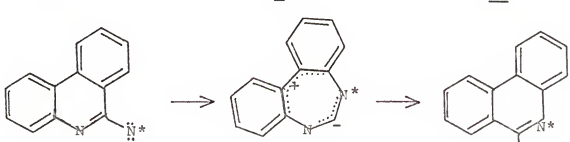

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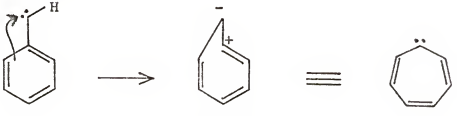
Although intermediates such as (9) or (12) are

somewhat difficult to understand, when applied to a carbocyclic carbene system the Wolff rearrangement (14) is seen to favor rearrangement of the bond with lower double bond character:



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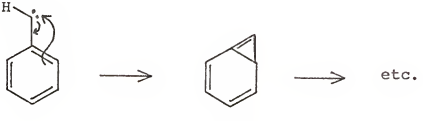
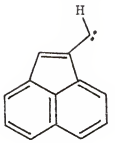
In contrast the bicycloheptatriene (4) would be expected to be formed from interaction with the bond of higher double bond character:



4

Making use of this characteristic, Mitsuhashi and Jones[14] in their investigation of naphthylcarbenes established that the carbene-carbene rearrangement proceeds through the bicycloheptatriene either as a reaction intermediate or a transition state. Further confirmation of this conclusion was found recently in acenaphthylcarbene (15) studied by Coburn and Jones.[15] The products isolated

were consistent with a rearranged carbene (15B) formed via



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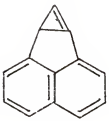
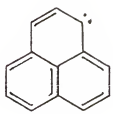


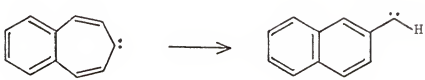
15A



15B

the fused cyclopropene (15A). The carbene (15B) cannot be obtained by a Wolff mechanism.

By 1972 in the full summary paper by Jones et al.[16] it had become widely assumed[1,2,5-10,14] that gas-phase carbene-carbene rearrangements were occurring through a reactive intermediate or transition state bicycloheptatriene. Further work soon appeared substantiating the generality of this mechanism. Krajca, Mitsuhashi, and Jones[17] reported the solution and low temperature rearrangement of benzocycloheptatrienylidene (16) to



16 17

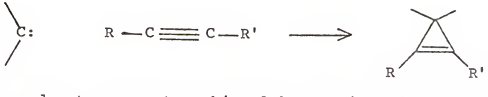
ß-naphthylcarbene (17) and Jones et al.[18] presented strong evidence for the first rearrangement of an arylcarbene to an aromatic carbene in solution.

At the inception of this work, though, all the evidence for the intermediacy or transition state nature of (4) had been indirect. The bicycloheptatriene had

been inferred from product analysis of the rearranged carbene and labeling experiments. But there had been no direct evidence for (4) either as an intermediate or as a transition state.

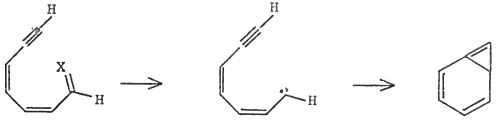
Thus the objective of this work was to gather direct evidence for the existence and properties of the oft-proposed bicycloheptatriene. As an initial basis and starting point, it was assumed (either by intuition or prejudice) that the bicycloheptatriene was indeed an intermediate. The most direct evidence, its isolation, was deemed too risky an adventure and so, its direct, unequivocal synthesis was undertaken. It was hoped that once made under the appropriate circumstances it would ring open to the carbene and products from the carbene would actually be isolated.

In order to avoid complications by strong base or acid present when the fused cyclopropene was formed, neutral conditions were investigated which had precedence for cyclopropene formation. The method decided on was the addition of a carbene to an acetylene.[19]



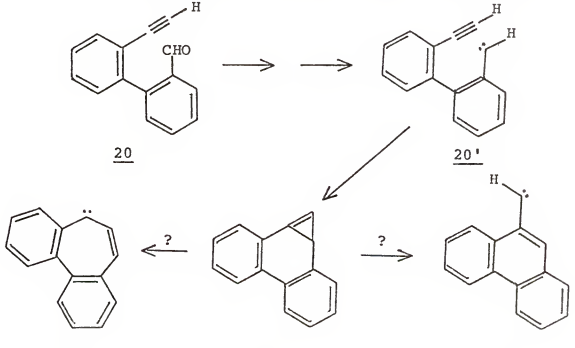
In order to generate a bicycloheptatriene from such a reaction the addition must be intramolecular in a system with an acetylene at one end of an open chain, a potential, neutral carbene precursor at the other, and

two conjugated cis double bonds in between, as depicted in (18).



18 19 4

The carbene precursor chosen was an aldehyde which could be converted to the tosylhyrazone sodium salt[20] and then either pyrolyzed or photolyzed to generate the carbene (19). In order to lock the double bonds into the cis conformation, they were annelated (20). This would generate carbene (20') which, if it added to the acetylene, would give the dibenzocycloheptatriene (21). Once formed



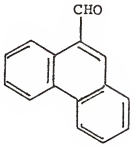
20 20' 22 21 23

(21) could then ring open to either dibenzocyclohepta-

trienylidene (22) or 9-phenanthrylcarbene (23). It was predicted, in light of the chemistry of (16),[17] that ring opening would go preferentially to (23).

RESULTS

All carbenes were generated either thermally or photolytically from the sodium salt of the appropriate tosylhydrazones.[16,20] Initially, this required three carbonyl compounds, 9-phenanthryl carboxaldehyde (24), 5H-dibenzo[a,c]cyclohepten-5-one (25), and 2-ethynylbiphenyl-2'-carboxaldehyde (26).



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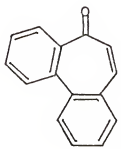

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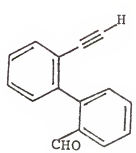

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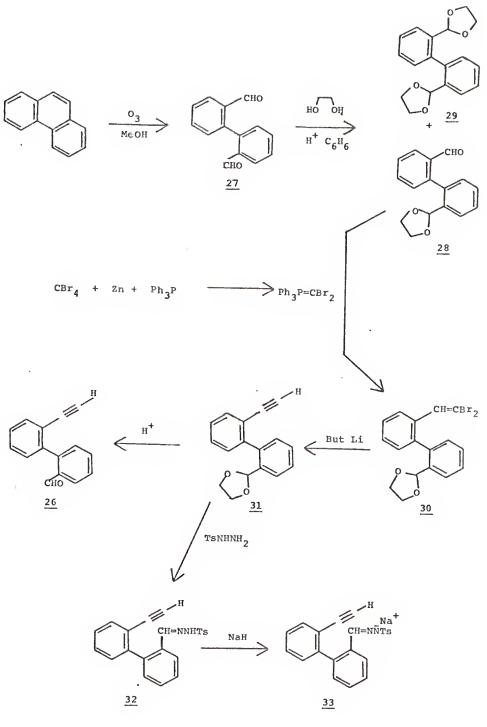
The ketone (25) was obtained as the tosylhydrazone sodium salt from T. T. Coburn[21] who was studying the resultant carbene concurrently with this work. The tosylhydrazone was prepared from commercially available[22] 9-phenanthryl carboxaldehyde and subsequently was converted to its sodium salt (24') (see Experimental). The synthetic scheme (scheme 1) was devised for the preparation of 2-ethynylbiphenyl-2'-carboxaldehyde (26).

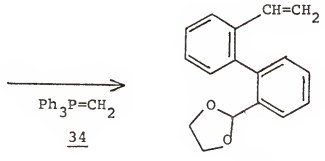

O3
MeOH
CHO
CHO
27
HO OH
H+ C6H6
29
+
CHO
28
CBr4 + Zn + Ph3P
Ph3P=CBr2
CH=CBr2
But Li
H+
CHO
26
31
30
TsNHNH2
CH=NNHTs
32
NaH
Na+
CH=NNTs
33

Scheme 1

Phenanthrene was ozonized by the procedure of Bailey and Erickson[23] to the known 2,2'-biphenyl dicarboxaldehyde (27) in 94% yield. 2-[2'-Formyl)-2-biphenylyl]-1,3-dioxolane (28) was prepared by the procedure of Robinson[24] from the dialdehyde (27) and ethylene glycol (one equivalent) refluxed in benzene with a catalytic amount of acid under a Dean-Stark water separator.

Examination of the crude reaction product mixture showed a singlet at δ9.79 (aldehyde H's of biphenydicarboxaldehyde (27); relative area: 1), a singlet at δ9.69 (aldehyde H of monoacetal (28); relative area 1), and two singlets at δ5.50 and δ5.48 (methine H's of monoacetal (28) and bisacetal (29); relative area collectively: 2)(cf. the benzylic methine H of 2-phenyl-1,3-dioxolane[25] appears at δ5.68). By allowing for the number of hydrogens per molecule giving rise to each signal, it was calculated the ratio of (27):(28):(29) was 1:2:1. (For instance, the two aldehyde signals were of equal area but there are twice the number of aldehyde hydrogens in (27) as in (28). Therefore there must be twice as much (28) as (27).) Attempts were made to increase the yield of monoacetal (28) -- e.g. longer reaction times, slower addition of ethylene glycol, more acid, no acid -- but in all cases the statistical distribution prevailed. Laborious column chromatography, however, gave a mixture containing about 90% monoacetal which was used directly in the next step.

Initially, methylene triphenylphosphorane (34) was added to the aldehyde (28) in the hope subsequent bromination, bisdehydrobromination would give the acetylene (31).



28 → ($Ph_3P=CH_2$, 34) → 35

The vinyl compound (35) was successfully made by this path and it did add bromine as evidenced by loss of red color. However, the dibromide of (35), as soon as it was formed, unmistakeably lost hydrogen bromide. This complicated the reaction immensely for cleavage of the ethylene acetal immediately commenced and the reaction deteriorated to intractable material.

Dibromomethylene triphenylphosphorane,[26] prepared from carbon tetrabromide, zinc dust, and triphenylphosphine, was then added to aldehyde (28). The vinyl dibromide (30), 2-[2'-(2,2-dibromovinyl)-2-biphenylyl]-1,3-dioxolane, was isolated in 84% yield. The dioxolane function was obvious from the nmr: δ5.48 (s, 1H) and 4.05-3.72 (m, 4H). The vinyl hydrogen was hidden in the aromatic region. The exact mass spectrum confirmed the molecular weight, formula, the presence of two bromine atoms as evidenced by the triplet[27] for the molecular ion, and reconfirmed

the acetal function by a very prominent M^+ -H peak, characteristic of acetals.[28] The terminal vinyl dibromide was very prominent in the ir by a band at 868 cm^{-1}. (cf. β,β-dibromostyrene,[29] 870 cm^{-1}).

Treatment of the dibromide (30) with 2.1 equivalents[26] of n-butyl lithium in tetrahydrofuran, followed by aqueous work-up, gave the acetylene, (31), 2-[2'-(ethynyl)-2-biphenylyl]-1,3-dioxolane, in 78% yield. It was obtained as a very viscous yellow oil. Crystallization could be induced by dissolving in ether and cooling to -78°C. However, after isolation of the crystals at that temperature when they were warmed to about -20°C, they melted. The aromatic protons of (31) were similar to (30) in the pmr but integrated to one less. The acetal protons were identical in both spectra; (31) also contained a very prominent singlet at δ2.89; the ir spectrum likewise confirmed the terminal acetylene showing absorptions at 3260 and 2315(w) cm^{-1}. (cf. phenyl acetylene:[30] δ3.08(s); 3280 and 2100(w) cm^{-1}.) The high resolution mass spectrum did not show a very intense molecular ion but the M^+ -H peak, characteristic of phenyl substituted 1,3-dioxolanes,[28] was very prominent.

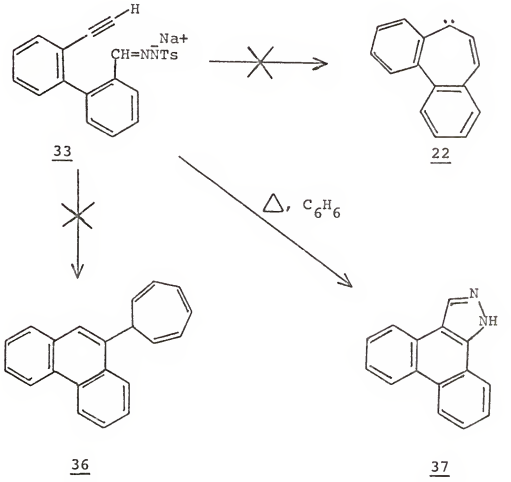
The acetylene acetal (31) could be hydrolyzed to the aldehyde (26) (all spectra consistent) but it was found unnecessary, as the tosylhydrazone (32) could be made directly from the acetal (31) in the manner[16] normally used for an aldehyde. The acetylene function

of the tosylhydrazone was readily apparent from signals in the nmr and ir: δ2.66; 3200 and 2105(w) cm^{-1}. The tosylhydrazone resisted all recrystallization attempts; however, the light yellow, powdery glass isolated after column chromatography gave a good elemental analysis and molecular ion in the mass spectrum. Other spectral characteristics were the singlet at δ2.39 for the tosyl methyl in the nmr, the broad N-H in the ir at 3280 cm^{-1}, and the S→O bands[31] in the ir at 1320 and 1165 cm^{-1}. One equivalent of sodium hydride was added to the tosylhydrazone in tetrahydrofuran under nitrogen to generate the salt (33). This sodium salt was very hygroscopic in air, turning to an oil in a few minutes.

When (33) was decomposed under various conditions, the 9-phenanthryl methine system was present in many of the products. In order to obtain authentic 9-phenanthrylcarbene products, (24') was decomposed first under conditions to which (33) would eventually be subjected. The products from reactions of (24') were carefully isolated and characterized. Reaction products of (33) were then compared with these now known, authentic compounds, independently prepared. In subsequent narration of reactions of salt (33), if 9-phenanthryl type products were obtained, those results will be preceded by a description of a similar reaction carried out with (24').

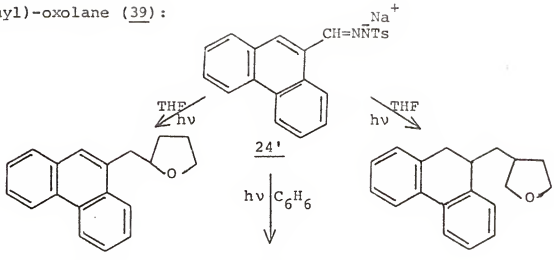
When thermally decomposed in benzene at 125°C the salt (33) did not give 9-phenanthrylcarbene products,

-- e.g. 9-(2,4,6-cycloheptatrien-1-yl)phenanthrene[32] (36), nor products from dibenzo [a,c]cycloheptatrienylylidene (22). Instead, known[33,34] 2H-phenanthro[9,10-c]pyrazole (37) was isolated in nearly quantitative yield.



Photolysis of (24') in benzene/tetrahydrofuran (1:2) at -60°C gave 6% of 9-(2,4,6-cycloheptatrien-1-yl) phenanthrene (36) and 9% of two inseparable isomeric products generated from C-H insertion of 9-phenanthrylcarbene (23) into tetrahydrofuran. These appeared to be 2-(9-phenanthrylmethyl)-oxolane (38) and 3-(9-phenanthryl-

methyl)-oxolane (39):



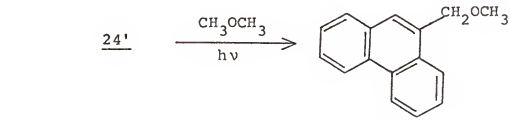
38 36 39

Evidence of two isomeric compounds came from careful TLC; two very close, overlapping spots were seen upon chromatography of material that gave acceptable elemental analysis. Corroboration of the gross structural features present in (38) and (39) was found in other spectral data.

An ir band at 1070 cm^{-1} is indicative of an ether linkage.[31] Large multiplets in the two regions 4.4-3.3δ and 1.8 in the nmr are characteristic of the α and β protons, respectively, of tetrahydrofuran. Integration of these two areas showed an approximate ratio of 5:4 and thus the benzylic type protons were presumed to be in the lower field multiplet. The rest of the spectrum is consistent with the phenanthryl nucleus as is the UV.

Photolysis of (33) in various mixtures of benzene and tetrahydrofuran at progressive lower temperatures gave, generally, increasing yields of (36), (38), and (39) and decreasing yields of pyrazole (37). The exact yields are contained in chart 1 (Experimental).

The photolytic decomposition of 9-phenanthryl carboxaldehyde tosylhydrazone sodium salt (24') in dimethyl ether at -60°C produced as the main product (40% isolated yield) 9-methoxymethyl phenanthrene (40).



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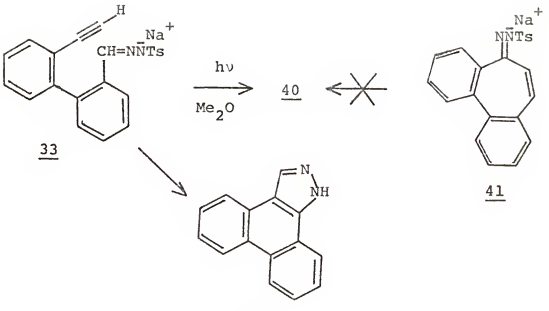
The unsymetrical ether linkage was evident in the ir by two bands[31] at 1190 and 1102 cm^{-1}. The pmr spectrum was very simple: δ3.45 (s, 3H, $-OCH_3$), 4.90 (s, 2H, benzylic methylene) and the phenanthryl aromatic hydrogens (cf. benzyl methyl ether[35] pmr: δ 3.29 (s, 3H), 4.35 (s, 2H); ir: 1200 and 1100 cm^{-1}). The ether (40) gave a good molecular ion in the mass spectrometer as well as a $M^+ -CH_5$ ($Ar-C\equiv O^+$) and $M^+ -OCH_3$. Elemental analysis was satisfactory.

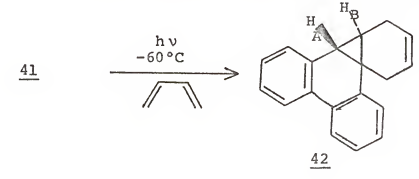
The tosylhydrazone salt (33) was irradiated in pure dimethyl ether at -110°C. Two major products were found: the pyrazole (37), 15%, and the methyl ether (40), 11% (isolated yields). Then the same reaction was run with the sodium salt of 5H-dibenzo[a,c]cyclohepten-5-one tosylhydrazone, (41), the presence of (40) could not be detected (limit of detection, combined TLC and micro nmr ∿0.05%). Material was found that contained



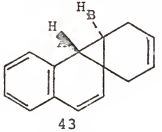
only aromatic protons; no attempt, however, was made to isolate or characterize this type of compound.

When the salt (33) was photolyzed in dimethyl ether at -110°C in the presence of a catalytic amount of triethylamine, the yield of the methyl ether (40) dropped to < 2% (a six-fold decrease). Conversely, the yield of pyrazole (37) more than doubled to 37%.

When 5H-dibenzo[a,c]cyclohepten-5-one tosylhydrazone sodium salt (41) was photolyzed in 1,3-butadiene at -60°C, the major product obtained was 8b,8c,9,12-tetrahydrobenzo[1,3]cyclopropa[1,2-l]phenanthrene (42).

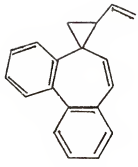


Two ir bands at 3068 and 1005 cm^{-1} (cyclopropane C-H stretch and cyclopropane ring deformation[36]) were indicative of a cyclopropane unit. The high resolution mass spectrum confirmed the molecular weight and formula. The pmr spectrum was not conclusive however, in that it was nearly identical with that reported[32] for 4,5-benzotricyclo[5.4.0.$0^{1,6}$]undeca-2,4,9-triene (43).



43

H_A and H_B in (42) were slightly downfield from their positions in (43): H_A of (42) unfortunetly appeared in the allylic multiplet at δ2.55; H_A of (43) appeared slightly above the allylic system at δ2.36 (allylic hydrogens at δ2.53); H_B of (42) was observed at δ0.7-0.4 while H_B of (43) was found at δ0.55-0.25. The multiplet pattern of H_B in (42) was nearly superimposable with H_B of (43) and coupling constants obtained agreed well; thus, the stereochemical assignments for (43) must also hold for (42). The unconjugated vinyl hydrogens of both compounds appeared at identical chemical shift (δ5.62) although those of (42) were more of a structured doublet than a multiplet. No spiro products such as (44) were detected.

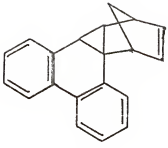


44

The salt (33) was photolyzed in approximately equal amounts of dimethyl ether and 1,3-butadiene at -110°C. Three products were obtained: the pryrazole (37). 30% ± 5%, the dibenzotricyclic compound (42), 5% ± 1%; and the methyl ether (40), 11% ± 2%. This experiment was repeated twice; the figures given were the average, isolated percent yields for the three duplicate runs.

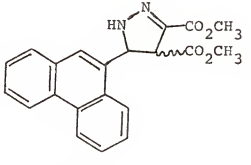
The photolysis of the salt (33) was performed again in approximately equal volumes of dimethyl ether and 1,3-butadiene at -110°C but also with a catalytic amount of triethylamine present. After usual work-up three products were obtained in the following isolated yields: pyrazole (37), 34%; methyl ether (40), 1%; olefin (42), 4%. A duplicate run was carried out with these results: pyrazole (37), 56%; methyl ether (40), 0.5%; olefin (42), 4%.

The salt (33) was also photolyzed in cyclopentadiene at -60°C. By comparison with authentic material, TLC and uv showed the reaction product mixture to contain less than 0.5% of the endo tricyclic olefin[32] (45).



45

9-Phenanthryl carboxaldehyde tosylhydrazone sodium salt (24') was decomposed in benzene at 125°C in the presence of an equimolar amount of dimethyl fumarate. The ir spectrum of the major material isolated after PTLC of the crude reaction mixture showed absorptions at 3360 (N-H), 1740 (ester) and 1560 cm^{-1} (C=N).[16,37] After the high resolution mass spectrum confirmed the molecular formula, the material was assigned structure (46), 3,4-dicarbomethoxy-5-(9-phenanthryl)-2-pyrazoline.



46

Repeated recrystallization from ethanol/water did not, however, effect a narrow melting point range. The best

range obtained, 5°, seemed too large for a single isomer and thus it was felt a mixture of stereoisomers was actually isolated.

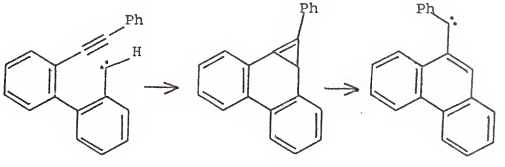
Verification of this was made by spectral comparisons with other pyrazolines.[16,37] In the ir the two different ester carbonyl absorptions are normally very obvious. In (46), those absorptions appeared at 1740 as a broad band (~30 cm^{-1} at half peak height) and a shoulder at 1743 cm^{-1}. In the nmr spectrum the N-H was seen as a broad singlet at δ6.9-6.4. The benzylic type proton at 4.85 was not the expected doublet but rather two overlapping doublets. The α-carbomethoxy proton was a multiplet at 3.95. Thus no coupling constant could be calculated between these latter two protons. Known pyrazolines show the ester methyl protons as two singlets spaced apart by 0.06 ppm. The pyrazoline (46) showed three singlets (at the proper chemical shift) within a range of 0.08 ppm and which integrated to a relative area of 6H.

When the same 9-phenanthryl carboxaldehyde tosylhydrazone sodium salt was photolyzed in dimethyl ether at -110°C with a large excess of dimethyl fumarate, the pyrazoline (46) was not isolated or detected. Instead a 43% yield of 9-phenanthryl carboxaldehyde was realized. This was the only component of the reaction mixture that could be identified.

Finally, when salt (33) was photolyzed under the above conditions, neither the pyrazoline (46) nor

9-phenanthryl carboxaldehyde was detected. The nmr spectra of material isolated after PTLC of the reaction mixture indicated the presence of dimeric or polymeric aromatic compounds, but these were not characterized further.

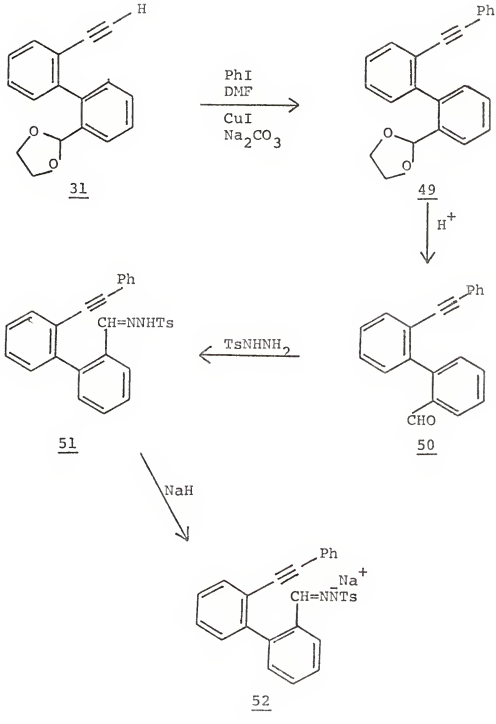
In an attempt to reduce the amount of pyrazole (37) obtained from reactions of (33), the terminal acetylene group was substituted with a phenyl ring. Carbene (47) then would be the new reacting species (in analogy with (20')). If (47) paralleled the reactions of (20'), products from 9-phenanthryl phenylcarbene (48) were to be expected. As in the case of carbenes (20') and (23) this meant studying reactions of (48) independently also.



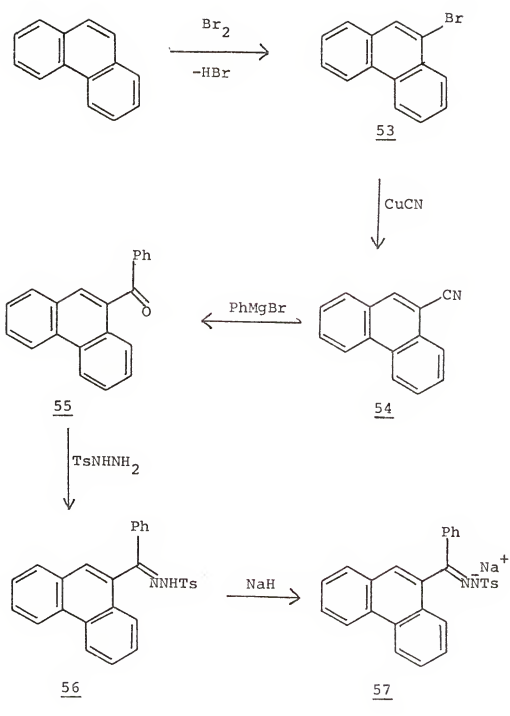
47 48

The above then necessitated two other synthetic schemes, II and III, to make the sodium salts of tosylhydrazones, (51) and (56), immediate precursors of carbenes (47) and (48), respectively.

Condensation[38] of phenyl iodide and (31) under the


H
PhI
DMF
CuI
Na_2CO_3
Ph
O
O
31
49
H^+
Ph
CH=NNHTs
$TsNHNH_2$
Ph
CHO
51
50
NaH
Ph
Na^+
$CH=\bar{N}NTs$
52

Scheme 2


Br2
-HBr
Br
53
CuCN
CN
54
PhMgBr
Ph
O
55
TsNHNH2
Ph
NNHTs
56
NaH
Ph
Na+
NNTs
57

Scheme 3

action of cuprous iodide and sodium bicarbonate in refluxing dimethylformamide resulted in the formation of the phenyl substituted acetylene (49), 2-[2'-(phenylethynyl)-2-biphenylyl]-1,3-dioxolane, in 60% yield. The acetylenic hydrogen signals of (31) were completely gone in the nmr and ir spectra. A sharp singlet appeared in the aromatic region of the nmr of (49), while in the ir a new band appeared at 695 cm^{-1}, indicative[39] of mono substituted benzene. The acetal function was still present in the nmr. The mass spectrum showed a molecular ion and a M^{+} -1. Elemental analysis was in excellent agreement with theory.

The acetal (49) was readily hydrolyzed to the aldehyde (50). The nmr spectrum of (50) showed an aldehyde proton at δ9.8 which was confirmed by the carbonyl absorption at 1685 cm^{-1} in the ir.

The tosylhydrazone (51), 2-(phenylethynyl)-biphenyl-2'-carboxaldehyde tosylhydrazone, was prepared by allowing the aldehyde (50) to react with tosylhydrazide (one equivalent) at room temperature and below for three days. It had all the properties expected except it could not be induced to crystalize. However, the glass obtained after column chromatography gave an excellent elemental analysis. The sodium salt (52) was isolated with no difficulty.

The synthesis of ketone (55) was accomplished by literature procedures[40,41,42] beginning with phenanthrene.

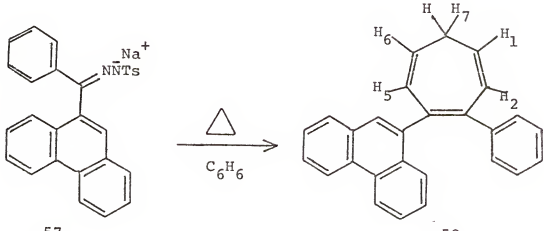
The ketone was converted to the tosylhydrazone (56) by refluxing with tosylhydrazide in ethanol. Its physical properties were consistent in all respects. The sodium salt (57) was easily prepared by reacting sodium hydride with (56) in tetrahydrofuran.

The same format that was followed with decompositions of (24') and (33) was duplicated with (52) and (57); i.e. salt (57) was decomposed first to obtain authentic materials derived from 9-phenanthryl phenylcarbene. Salt (52) was then run and the products obtained were compared with independently prepared materials.

The salt (57) was heated in benzene at 125°C. A red color immediately was formed and after twenty minutes had turned to yellow. Two products were isolated by PTLC. The first, a hydrocarbon by ir, was a one to one adduct of the carbene (48) and benzene as shown by a very intense molecular ion in the high resolution mass spectrum. The nmr spectrum showed a multiplet, almost a triplet, at δ3.1 (2H), two multiplets at 6.2-6.0 and 5.7-5.4, each 2H, as well as two aromatic multiplets at 7.7-6.8, (12H) and 8.6 (2H). The latter two multiplets indicated a 9-phenanthryl nucleus plus additional aromatic protons.

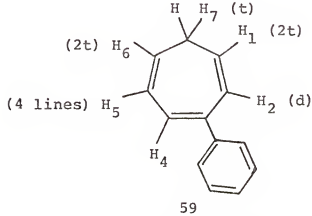
The structure that best agrees with the pmr data then is a cyclohepatriene substituted with a 9-phenanthryl group and a phenyl group. Although the exact substitution pattern cannot be unequivocably assigned, the best fit is

compound (58), 4-(9-phenanthryl)-3-phenyl-1,3,5-cycloheptatriene.



57 58

$H_{1,6}$ δ5.7-5.4(m)
$H_{2,5}$ δ6.2-6.0(m)



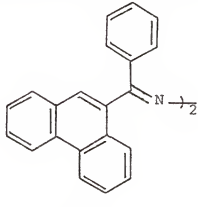
59

$H_{1,6}$ δ5.65-5.2
$H_{2,5}$ δ6.4 -6.1
H_7 δ2.23
H_4 δ6.83

This assignment was made mainly on the symmetrical distribution of protons in the vinyl and allylic multiplets and as well as the splitting patterms within the allylic multiplet. Although (58) does posses some symmetry the two aryl groups are sufficiently dissimilar to cause

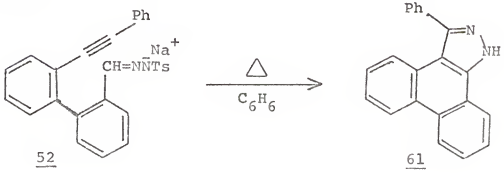
expected simple splitting patterns to become multiplets. The effect is experienced least in those protons furthest from the substitution, i.e. the allylic hydrogens. These appeared nearly as a triplet with finer, multiplet type splitting superimposed. The vinyl hydrogens agreed very well in chemical shift correlations with known 3-phenylcycloheptatriene (59).[43]

The second compound was more easily identified as 9-benzoyl phenanthrene azine (60). All spectra, including high resolution mass, were consistent. Yields after recrystalization of (58) and (60) were 22 and 55%, respectively.



60

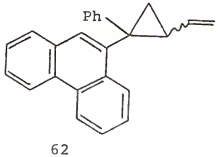
The thermal decomposition of salt (52) was carried out in benzene at 125°C. The known[44] pyrazole (61) 3-phenyl-2H-phenanthro[9,10-c]pyrazole, was isolated in 94% yield.



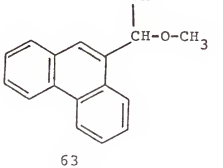
52 61

The presence of the cycloheptatriene (58) could not be detected by nmr, TLC, or PTLC. The photolysis of (52) in benzene at 10°C gave 75% of the pyrazole (61) and 5.5% of (58).

The photolysis of salt (57) in approximately equal volumes of dimethyl ether and 1,3-butadiene at -110°C gave two products. The first, isolated in 59% yield, was a cis and trans mixture of 1-(9-phenanthryl)-1-phenyl-2-vinyl cyclopropane (62). The ir spectrum showed bands at 3040, 1035 (cyclopropane[36]), 751, 702 (monosubstituted benzene[39]), 1450, 900, and 724 cm^{-1} (terminyl vinyl[39]). The nmr spectrum showed the 9-phenanthrene nucleus. The vinyl protons at δ5.45-4.75 (3H) were an unsymetrical multiplet as if these were two overlapping terminal vinyl groups. A broad multiplet at 2.8-2.2 (1H), cyclopropyl vinyl,[45] and another, more well-defined multiplet at 2.0-1.2 (2H), cyclopropyl,[45] completed the spectrum.



62

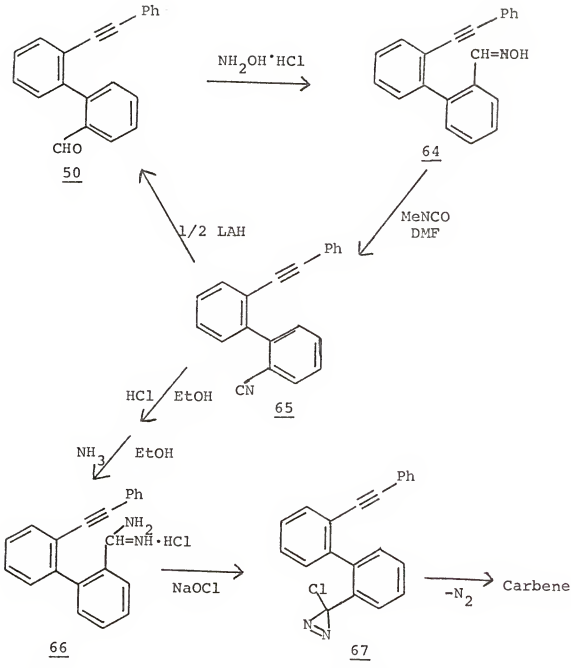


63

The second, isolated in 7% yield, was identified as the ether (63), 9-(methoxyphenylmethyl)-phenanthrene. All spectra compared favorably with those obtained for (40). The high resolution mass spectrum gave the correct molecular formula. Bands at 750 and 700 cm^{-1} in the ir confirmed the monosubstituted benzene.[39] The methine proton was seen at δ5.86 (s, 1H).

The photolysis of (52) was performed at -110°C in approximately equal volumes of dimethyl ether and 1,3-butadiene. Three products were isolated and were identified as the pyrazole (61), 48%, the cyclopropane (62), 6.7%, and the methyl ether, (63), 1%. A duplicate photolysis was run in the presence of triethyl amine. The yields of the same three products isolated did not change appreciably. Dimeric or polymeric aromatic compounds were seen in the nmr of other chromatographed (PTLC) material isolated from both reactions. These compounds, though, were not further characterized.

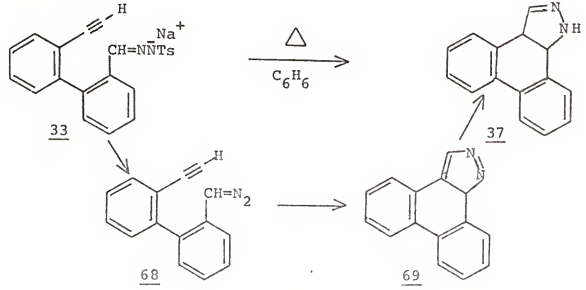
In an attempt to synthesize an alternate, neutral carbene precursor, the aldehyde (50) was converted[46] to the nitrile (65) via the oxime (64). It was hoped the nitrile could be converted to the amidine salt (66) by the method of Pinner[47] and then oxidized[48] to the chlorodiazirine (67). Unfortunetly, it was soon realized the salt (66) was going to be too difficult to make to warrant further work and, thus, the nitrile that had been synthesized was reduced back to the aldehyde (50). The



oxime (64) and the nitrile (65) were consistent in their properties as compared to model compounds, benzaldehyde oxime[49] and benzonitrile.[50]

DISCUSSION

Although the pyrolysis of tosylhydrazone sodium salts is a standard method[51] of carbene generation, the pyrolysis of (33) led only to a nitrogen containing compound, the pyrazole (37). Since tosylhydrazone sodium salts decompose[52] first to the diazo alkane by loss of sodium p-toluenesulfinate, the formation of the biphenyl diazo alkane (68) is assumed. Even though the reaction conditions should have been vigorous enough to cause loss of nitrogen,[52] from the exclusive formation of (37) it is apparant that the diazo group undergoes an intramolecular 3 + 2 cycloaddition with the very well-situated triple bond to give the pyrazolenine (69). Tautomerization of (69) results in the more stable isomer (37).



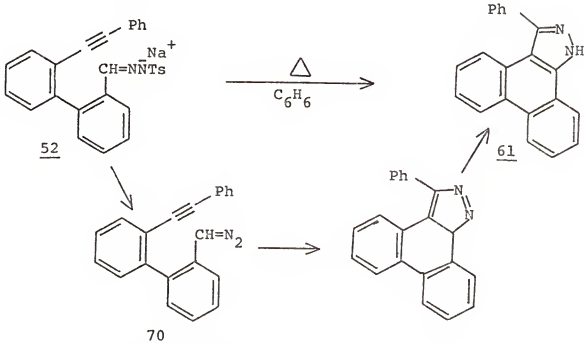
Intermolecular 3 + 2 cycloadditions of diazo alkanes and acetylenes are well documented as are the intramolecular electrocylic reactions of vinyl diazo alkanes (Eq. 1.).[53,54,55,56] Since the diazo group

Eq. 1

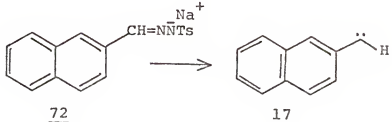
and double bond are directly bonded this latter reaction yields a pyrazolenine also. Although ring closure of (68) to form the pyrazolenine is intramolecular, it does require one more degree of unsaturation than expressed in Eq. 1, since the two reacting groups are separated by more than one bond. To the best of our knowledge this is the first example of this type of cycloaddition to give a pyrazolenine. However, this was not the intent of this work and our attention was directed to ways of minimizing pyrazole formation and promoting carbene formation.

Cycloadditions are known to be subject to steric constraints.[57] Thus the terminal acetylene carbon was substituted with a phenyl group in the hope the rate of the cycloaddition would be slowed down enough to allow the intermediate diazo alkane to loose nitrogen. When the tosylhydrazone sodium salt (52) was thermally decomposed only the nitrogen containing pyrazole (61) was isolated. In view of the nearly quantitative yield of (61), even in

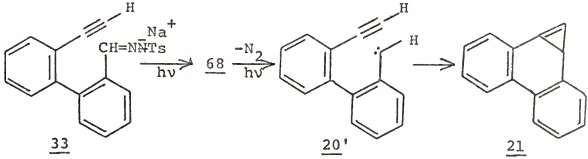
the case of the sterically hindered diazo alkane (70), the 3 + 2 cycloaddition must be an extremely facile reaction at elevated temperature.



Photolysis of tosylhydrazone sodium salts is also[51] a general procedure for carbene generation with the added advantage of permitting formation of the carbene at lower temperatures. For example, a temperature of 125°C was required to thermally generate carbene (17) from the sodium salt (72).[16]

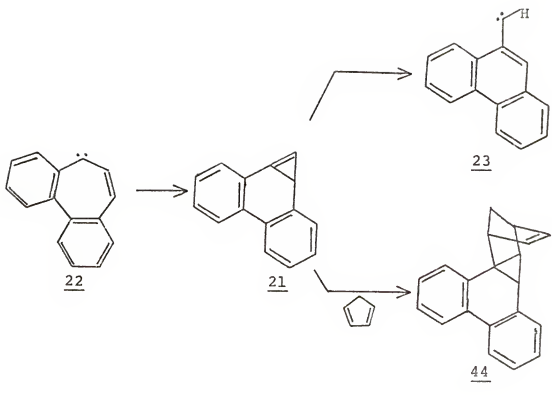


The temperature could be lowered to -30°C and under photolytic conditions the same carbene was formed. Thus, if a fast thermal reaction such as the 3 + 2 cycloaddition was removing a carbene precurson (the diazo alkane (68)) from the reaction medium before it itself could be thermolyzed to the carbene, a low temperature photolysis may generate the desired carbene (20'). It was hoped that photolysis would form the diazo alkane (68) but the low temperature would retard the cycloaddition enough to permit absorption of a second photon which would cause loss of nitrogen to give carbene (20') which would close to (21).



33 20' 21

It was originally proposed (see Introduction) that (21) would be evidenced by products from 9-phenanthryl-carbene. However, concomitant with this work, Coburn and Jones[32] developed a system which effectivily traps (21) when generated from (22) in its rearrangement to (23). It was reported that if (22) is formed either thermally or photolytically in the presence of cyclopentadiene, (21) is diverted from ring opening and undergoes the

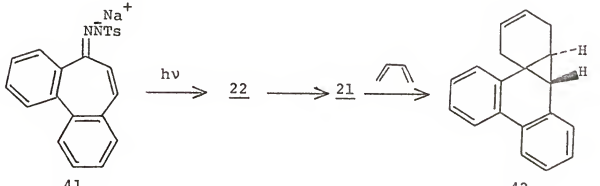


Diels-Alder reaction with the diene to give (44).

Accordingly, (33) was photolyzed in neat cyclopentadiene at -10°C. Although these were conditions that successfully trapped (21) from (22), none of the adduct (44) was detected upon irradiation of (33). Again only pyrazole (37) was identified in the reaction mixture. In spite of this disappointing result we still felt quite strongly that carbene (20') could be formed photolytically if the temperature were low enough.

Therefore special equipment was designed and built that would permit photolysis as low as -120°C in solution (see Experimental). However, the freezing point of cyclopentadiene mitigated against trapping experiments at that temperature with that diene. Therefore, 1,3-butadiene

was employed as the diene and solution was effected by addition of an equal volume of dimethyl ether. However, (22) had not been studied photolytically in butadiene nor at such low temperature. This necessitated then an investigation of (41) under these conditions. Photolysis of (41) in butadiene and dimethyl ether led to adduct (42) in 30% yield. The trans configuration of the cyclopropane hydrogens argues very well for cyclopropene trapping by butadiene in a concerted 4 + 2 manner. There is no example of the formation of any other[58,59,60] isomer with stereochemistry different than shown in (42) in Diels-Alder reactions of similar cyclopropenes with dienes.

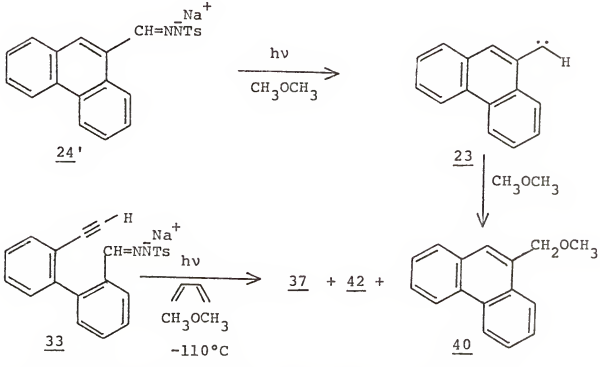


41 42

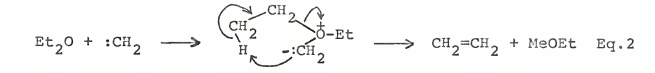
Finally, then, the photolysis of (33) under the same low temperature conditions resulted in the isolation of the same adduct (42). The appearance of (42) in this reaction requires the intermediacy of the dibenzobicycloheptatriene (21). Thus it appeared that (21), the oft-proposed bicycloheptatriene of aryl carbene-aromatic carbene rearrangements, had been independently synthesized from the low temperature photolysis of (33) presumably

from the addition of carbene (20') to the internal acetylene function. (Note: scheme on page 47 describes all compounds and reactions of (33).)

In addition to the Diels-Alder adduct (42), the low temperature photolysis of (33) at -110°C gave also the ether (40). This same compound was also isolated

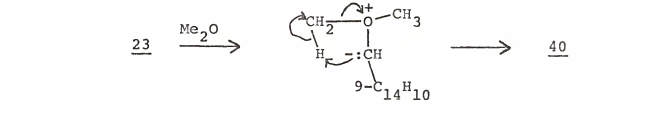


as the major component when 9-phenanthryl carbene (23) was generated independently in neat dimethyl ether. Therefore (40) is presumed to arise from reaction of dimethyl ether and 9-phenanthrylcarbene (23). Ether (40) is unusual in that there has been loss of methylene from the carbene and dimethyl ether. Ethers are known to react with carbenes through an oxygen ylid.[61] If fragmentation is observed it usually proceeds through β hydrogen abstraction and olefin elimination (Eq. 2):



Eq.2

However, in the case of (23) and dimethyl ether, the ylid must α eliminate and lose methylene; the fate of the latter is unknown.[62] (Note: the formation of (40) from (23) when generated from (22) mitigates against (40) arising from reaction of solvent with 9-phenanthryl diazo methane.)

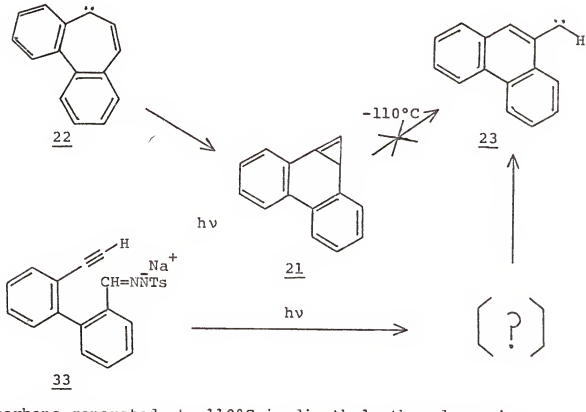


In any respect the appearance of (40) from (33) indicates that 9-phenanthrylcarbene (23) is formed at -110°C from the photolysis of (33).

It was also reported by Coburn and Jones[32] that if dibenzocycloheptratrienylide (22) is generated at -50°C in the absence of dienes, products are isolated that are derived from 9-phenanthrylcarbene (23). It was also presummed that (23) arose from rearrangement of (22) via (21), now known to be an intermediate.

However, in our hands, it was noted that photolysis of (22) at -110°C in pure dimethyl ether (no diene present) did not give rise to (40) nor any other products attributable to 9-phenanthrylcarbene (23). (Purely aromatic type compounds were observed and were presummed to be dimeric or polymeric. There was no indication that these arose from (23).)

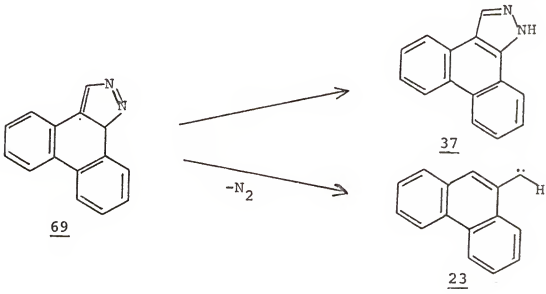
This apparant dichotomy can only be rationalized if (23) does not originate from (21) at -110°C. It was evident, from lack of formation of (40), that (21) simply did not ring open to (23) at -110°C. (9-Phenanthryl-



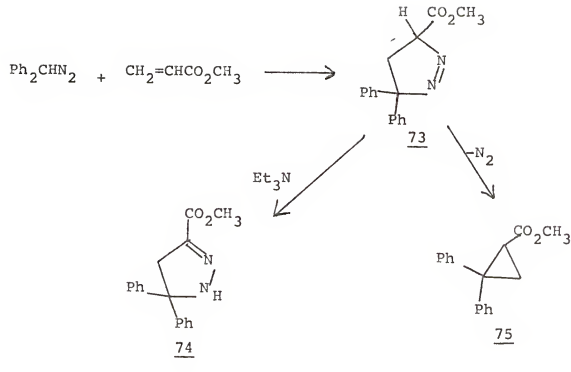
carbene generated at -110°C in dimethyl ether does give (40).) This then was the first time a carbene-carbene rearrangement was halted in midstream by simply a decrease in temperature. Furthermore, 9-phenanthrylcarbene (23) observed in the photolysis of (33) must be produced from some other intermediate in the reaction sequence.

The photolytic or thermal loss of nitrogen from pyrazolenines (3H-pyrazoles) to give vinyl carbenes is very well-documented in the literature.[53,54,55] In fact, this decomposition has become one of the major ways to

generate vinyl carbenes.[63] The immediate precursor (69) to pyrazole (37) is a pyrazolenine and since (37) is always produced in reactions of (33), could (69) be the source of extraneous 9-phenanthrylcarbene (23) (a vinyl carbene)? The pyrazolenine (69) could be partitioned between isomerization to (37) and loss of nitrogen to (23).



Although the tautomerization of (69) to (37) is a thermally allowed 1,5sigmatropic hydrogen migration,[64] isomerization of pyrazolenines to pyrazoles (and also 1-pyrazolines to 2-pyrazolines) is known to be subject to subtle acid/base changes.[33,44,65] For example, the 2-pyrazoline (74) is isolated in high yield when the 1-pyrazoline (73) is formed in the presence of triethylamine. In the absence of base (73), when formed from diphenyldiazomethane and methyl acrylate spontaneously loses nitrogen to give the cyclopropane (75).



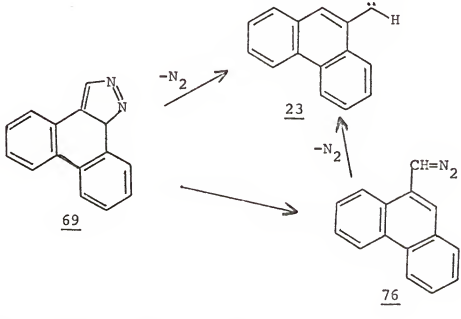
Accordingly, the photolysis of (33) at -110°C in dimethyl ether was conducted in the presence of triethyl amine. The effect was dramatic. The yield of ether (40) fell from 11% to less that 2% while the amount of pyrazole (37) more than doubled. This result implicates (69) as the source of 9-phenanthrylcarbene (23).

There are two widely held mechanisms for generation of vinyl carbenes from pyrazolenines. The first involves loss of nitrogen from the pyrazolenine to give the carbene directly. Closs[66] has recently concluded that such a path might be very important especially when high energy radiation is used.

The second proposes an electrocyclic ring opening of the pyrazolenine which gives rise to a vinyl diazo

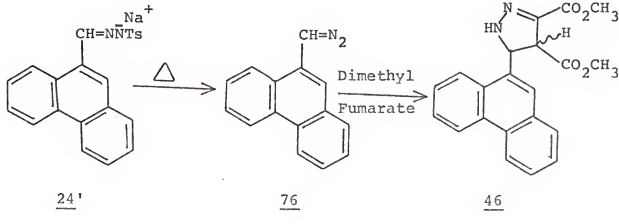
alkane; subsequent loss of nitrogen generates the carbene. Support for this mechanism comes from the few instances in which the diazo alkane was actually isolated.[67]

When these two mechanisms are applied to the decomposition of (69) it is noted that in the second path 9-phenanthryl diazo methane (76) is formed. Attempts

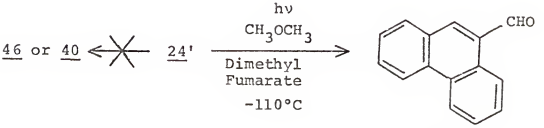


were therefore made to intercept (76).

For purposes of comparison, salt (24') was thermally decomposed in dimethyl fumarate to give the pyrazoline (46).



Photolysis of (24') at -110°C in dimethyl ether with excess dimethyl fumarate did not give (46) or (40) but rather almost 50% of 9-phenanthryl carboxaldehyde (24).



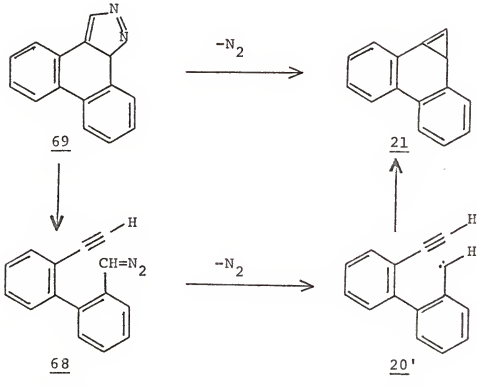
24

Although this is an atypical reaction of tosylhydrazone sodium salts, (33) was photolyzed under as identical conditions as possible as above. Only dimeric or polymeric aromatic material was isolated. Neither (46), (40), (24) or any other singularly identifiable material was isolated.

Thus from lack of any parallel between the two reactions it is cautiously suggested that (23) arises from a direct loss of nitrogen from (69). However, since the first photolysis gives very unusual results and the second negative results, a definite conclusion concerning the mechanism of decomposition of (69) to (23) cannot be made.

One further complication does exist in the photolytic decomposition of (33). A mechanism can be envisaged that invokes bicycloheptatriene (21) formation from the pyrazolenine (69) either by direct loss of nitrogen or reversal of (69)

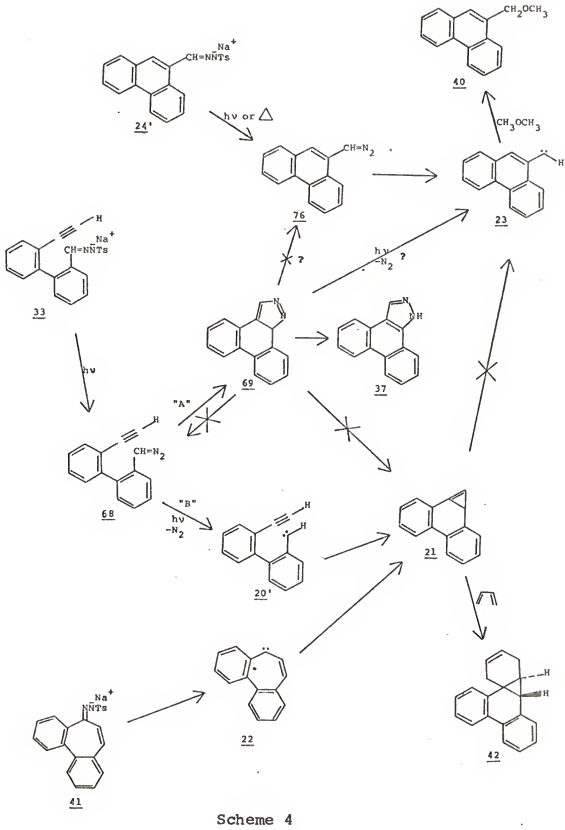
back to the biphenyl diazo methane (68) which looses nitrogen to give the carbene (20') which adds to the triple bond, forming (21).



69 21 68 20'

However, when (33) was photolyzed in dimethyl ether and 1,3-butadiene at -110°C in the presence of triethyl amine, the yield of the Diels-Alder adduct (42) was unchanged within experimental error. The ether (40) experienced the same dramatic decrease in yield and likewise pyrazole (37) formation was up, just as in the other reaction of (33) with triethyl amine present. This mitigates well against the pyrazolenine (69) as a bicycloheptatriene (21) precursor.

In summary (see page 47) then it is concluded that, at -110°C in dimethyl ether and 1,3-butadiene, (33)



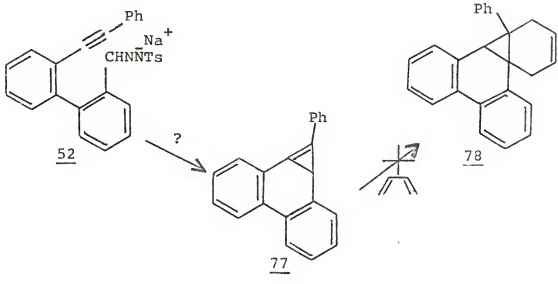
Scheme 4

undergoes photolysis according to the following scheme: the biphenyl diazo methane (68) is formed and is partitioned into two reaction paths. Path A is a cycloaddition to the pyrazolenine (69). Path B is a subsequent photolysis that causes loss of nitrogen and formation of carbene (20'). The latter adds to the acetylene and gives rise to dibenzobicycloheptatriene (21), an intermediate that can be trapped with butadiene. This same intermediate is also generated from carbene rearrangement of (22). At this temperature (21) does not open to (23). This is the first example of a carbene-carbene rearrangement that was stopped in midstream by a simple temperature decrease.

Products derived from reaction of 9-phenanthryl-carbene (23) with solvent can be rationalized by formation of (23) from photolysis of pyrazolenine (69) possibly from a concerted loss of nitrogen. There is no evidence that implicates 9-phenanthryl diazo methane (76) in the formation of (23) from (69). The pyrazolenine (69) does not contribute to the synthesis of the bicycloheptatriene (21). Lastly, of course, the pyrazolenine (69) can tautomerize to the pyrazole (37) which actually is the major reaction pathway.

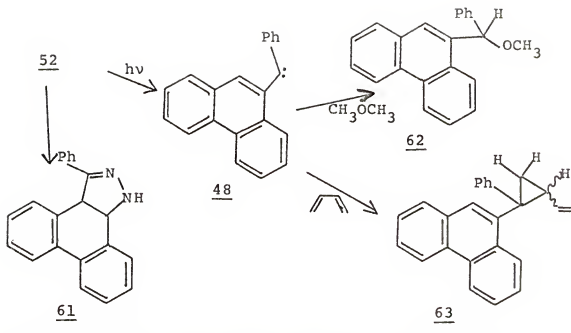
The phenyl substituted system (52) under the same photolytic conditions as (33) does not lead to any Diels Alder type products such as (78). Perhaps the phenyl group sterically hindered the reaction or possibly the substituted cyclopropene is not as reactive towards

butadiene as (21) at that temperature. At this time a definite conclusion cannot be drawn concerning the fate of

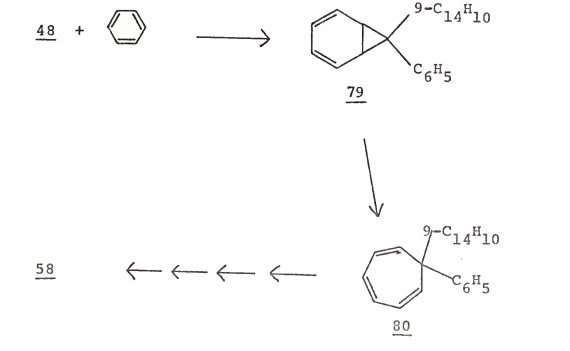


the phenyl substituted bicyclcoheptatriene (77). In addition to the phenyl pyrazole (61), products were also isolated from 9-phenanthryl phenylcarbene (48) upon photolysis of (52) in dimethyl ether and 1,3-butadiene. Ether (62) and cyclopropane (63) were formed in 7 and 60%, respectively. It is interesting to note that (48) reacts much more favorably with butadiene than dimethyl ether. The opposite is true for 9-phenanthrylcarbene (23). In fact (23) did not react with butadiene to any detectable extent.

Reaction of (48) with benzene leads to a cycloheptatriene (58) as expected but the substitution of the latter was surprising. Presumably (48) adds to benzene to give the norcaradiene (79) which ring opens



to the 7,7-diaryl cycloheptatriene (80). The product (58) can then be explained by a series of successive, facile, 1,5 sigmatropic hydrogen or aryl shifts occurring in this order: phenyl, hydrogen, 9-phenanthryl, hydrogen. Although the sequence is unusual, the individual migrations are not unprecedented.[68]



Of course, without direct evidence for (77), the mechanism by which carbene (48) is formed is purely speculative. The photochemistry of (52) could parallel (33) but all facets of the latter's chemistry are neither implied or necessary.

EXPERIMENTAL

General. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia. Nuclear magnetic resonance spectra (nmr) were obtained on a Varian A60-A spectrometer. Samples were dissolved and run in deuterochloroform unless otherwise noted. Chemical shifts are reported in delta (δ) values from internal tetramethylsilane standard. Low resolution mass spectra were determined on a Hitachi model RMU-6E mass spectrometer. High resolution accurate mass spectra were determined on a AEI MS-30 Double Beam Mass Spectrometer. Infared spectra (ir) were obtained on Beckman IR-10 instrument with absorptions reported in reciprocal centimeters (cm^{-1}). Ultraviolet spectra were obtained on a Cary 15 double-beam spectrophotometer using 1-cm quartz cells with absorption maxima reported in nanometers (nm).

All chemicals used were reagent grade unless otherwise specified. Tetrahydrofuran and diethyl ether were dried by passage through a 2.5 cm x 40 cm column of Woelm basic alumina-activity grade I. The first 150 ml of solvent were discarded; the next 1000 ml were

collected and stored over calcium hydride in previously dried (150°C, 4 hr) amber bottles. Analytical thin layer chromatography (TLC) was accomplished on 2" x 8" glass plates coated in these laboratories with 0.25 mm layer of E. Merck HF-254 silica gel. Spreading slurry was made by vigorously shaking 30 g of silica gel with 65 ml water and 10 ml methanol until the mixture was consistently smooth. Preparative thin layer chromatography plates (PTLC) were made on 8" x 8" glass plates coated with 1.0 mm layer of E. Merck HP-254 silica gel. Coating slurry was prepared as above except substituting these amounts: 96 g preparative silica gel, 220 ml water, 20 ml methanol. Components were visualized by their quenching of fluorescence under uv light.

Whenever possible column chromatography was performed in quartz columns. Compounds were visualized by their quenching or enhancement of flourescence of the column under short wave length (254 mμ) ultra-violet light. The usual commercial grade adsorbents were made fluorescent by the addition of 1% by weight of E. I. duPont de Nemours and Co. # 609 fluorescent material which was dispersed evenly by vigorously stirring a slurry of the latter and former in the eluting solvent. The column was then packed with this material directly.

2,2'-Biphenyl Dicarboxaldehyde (27). Phenanthrene was ozonized according to the procedure of Bailey and Erickson.[23] Yield 94%. mp: 52-54°. Lit.[23] 56°C. The

reaction can be scaled up by a factor of ten with no adverse problems.

2-[2'-(Formyl)-2-Biphenylyl]-1,3-Dioxolane (28). 2,2'-Biphenyl dicarboxaldehyde (27) (51.5 g, 0.245 mol) was dissolved in 500 ml benzene. To this solution was added ethylene glycol (15.2 g, 0.245 mol) and a catalytic amount[24] of p-toluenesulphonic acid (0.1 g). This mixture was refluxed overnight (16 hr) employing a Dean-Starke trap to remove azeotroped water. After cooling to room temperature the solution was extracted successively with 5% sodium bicarbonate solution (2 x 100 ml), water (2 x 100 ml), saturated sodium sulfate solution (2 x 100 ml) and dried over anhydrous sodium sulfate. After removal of the benzene by rotary evaporator, 67 g of a yellow oil remained. This was shown by nmr to be a statistical distribution of unreacted dicarboxaldehyde: monoacetal:bisacetal :: 1:2:1; pmr of mixture: ($CDCl_3$) δ9.79 (s, 2H), 9.69 (s, 1H), 8.0-7.0 (m, 24H), 5.50 and 5.48 (2 Singlets, 3H), 4.0-3.5 (m, 12H). Various attempts at trying to increase the proportion of mono-ethylene acetal (rate of addition, reaction time, etc.) were unsuccessful. Column chromatography over silica gel eluting with 95% pentane, 5% ether gave a mixture containing about 90% monoacetal. This material was used directly in the following.

2-[2'-(2,2-Dibromovinyl)-2-Biphenylyl]-1,3-Dioxolane (30). To the black, dry methylene chloride

solution of dibromomethylene triphenylphosphorane (0.06 mol) prepared a day previous by the method of Corey and Fuchs[26] was added a 50 ml methylene chloride (dried by distillation from P_2O_5) solution of 7.83 g (0.03 mol) of the 2-[2'-(formyl)-2-biphenylyl]-1,3-dioxolane (28) prepared above. The reaction was stirred for 24 hours under nitrogen and worked up by the procedure of Corey and Fuchs.[26] After concentrating the pentane-methylene chloride extracts on a rotary evaporator, the yellow residue was chromatographed over silica gel (elution with 85% pentane, 15% ether) to give the dibromide which was recrystalized from ether at -15°C. Mp 75-76°; yield 84%; ir (Nujol mull, NaCl plates): 2853, 1690, 1595, 1380, 1275, 1250, 1121, 1070, 982, 963, 944, 868, 822, 798, 773, 758 cm^{-1}; pmr ($CDCl_3$) δ7.81-7.04 (m, 9H), 5.48 (s, 1H), 4.05-3.72 (m, 4H).

mass spectrum:

For:	Calcd: m/e	Found: m/e
$C_{17}H_{14}O_2{}^{81}Br_2$	411.9319	411.9332
$(C_{17}H_{14}O_2{}^{81}Br_2)$-H	410.9240	409.9277
$C_{17}H_{14}O_2{}^{81}Br{}^{79}Br$	409.9339	409.9375
$(C_{17}H_{14}O_2{}^{81}Br{}^{79}Br)$-H	408.9261	408.9273
$C_{17}H_{14}O_2{}^{79}Br_2$	407.9359	407.9378

2-[2'-(Ethynyl)-2-Biphenylyl]-1,3-Dioxolane (31)

2-[2'-(2,2-Dibromovinyl)-2-biphenylyl]-1,3-dioxolane (30) (6.942 g, 0.0169 mol) was dissolved in 150 ml of dry

tetrahydrofuran under nitrogen. The solution was mechanically stirred and cooled in dry-ice/isopropanol bath and 16.3 ml of n-butyl lithium in hexane (2.17M, 0.0355 mol, 2.1 equiv) were added slowly. The solution turned from yellow to black. The reaction was allowed to gradually warm to room temperature overnight with stirring after which time the solution was yellow again. Water was cautiously added (50 ml), the mixture was poured into 1.5 l. water, and then extracted with ether (4 x 100 ml). The combined ethereal extracts were washed with saturated sodium sulfate solution (2 x 50 ml) and dried over anhydrous magnesium sulfate. After the ether was removed on a rotary exaporator, the yellow oil was chromatographed over silica gel eluting with 90% pentane, 10% ether. 2-[2'-(Ethynyl)-2-biphenylyl]-1,3-dioxolane (31) (3.228 g) was isolated as a very viscous yellow oil in 78% yield. Crystals could be obtained by dissolving in ether and cooling to -78°C. However, attempts to isolate the crystals at room temperature resulted in the original yellow oil. Ir (neat, NaCl): 3260, 3024, 2900, 2315(w), 1460, 1429, 1381, 1253, 1196, 1110, 1063, 954, 930, 749 cm^{-1}; pmr ($CDCl_3$) δ7.8-7.1 (m, 8H), 5.66 (s, 1H), 4.0-3.5 (symmetrical multiplet, 4H), 2.89 (s, 1H); mass spectrum: Found: m/e 249.0915 (Calcd for $C_{17}H_{14}O_2$: m/e 249.0915).

2-Ethynylbiphenyl-2'-Carboxaldehyde (26).

2-[2'-(Ethynyl)-2-biphenylyl]1,3-dioxolane (31) (1.0 g,

4 mmol) was dissolved in 20 ml of methanol. Five ml of 10% hydrochloric acidwere added and stirred for 30 minutes. The cloudy solution was poured into 100 ml of water and extracted with methylene chloride (3 x 20 ml). The organic extracts were combined and washed succesively with 5% sodium bicarbonate solution (2 x 30 ml), water (1 x 50 ml), saturated sodium sulfate solution (2 x 50 ml) and dried over anhydrous magnesium sulfate. After removal of methylene chloride by rotary evaporator the yellow oily residue was chromatographed over silica gel eluting with 95% pentane, 5% ether. The very light yellow, liquid aldehyde was isolated after solvent removal (1.76 g, 95%). Ir (neat, NaCl): 3270, 3043, 2920, 2840 2740, 2090(w), 1680, 1590, 1460, 1429, 1380, 1265, 1235, 1188, 1150, 1100, 995, 824, 750, 640 cm^{-1}; pmr ($CDCl_3$) δ10.66 (s, 1H), 8.0-7.8 (m) and 7.7-7.2 (m) (8H), 2.94 (s, 1H); mass spectrum: Found: m/e 206.0733 (Calcd for $C_{15}H_{10}O$: m/e 206.0731).

2-Ethynylbiphenyl-2'-Carboxaldehyde Tosylhydrazone (32). 2-[2'-(Ethynyl)-2-biphenylyl]-1,3-dioxolane (31) (2.948 g, 0.0118 mol) was dissolved in 50 ml absolute ethanol. Tosylhydrazide (2.198 g, 0.0118 mol) and one drop of concentrated sulfuric acid were added. The solution was then refluxed for 30 minutes. After cooling to room temperature, the solution was poured into 300 ml of water and extracted with methylene chloride (3 x 100 ml).

The organic extracts were combined and washed with saturated sodium sulfate (3 x 100 ml) and then dried over anhydrous magnesium sulfate. The yellow oil which remained after solvent removal was chromatographed over silica gel eluting with methylene chloride. A light yellow, powdery glass (4.231 g, 95%) resulted after drying overnight under vacuum. The tosylhydrazone resisted all attempts to crystallize it. Ir (neat, NaCl): 3280, 3200, 3060, 2920, 2105(w), 1515, 1430 (b), 1360, 1320, 1165, 1050 (b), 940, 830, 810, 760 cm^{-1}; pmr ($CDCl_3$): δ8.1-7.0 (m, 14H), 2.66 (s, 1H), 2.39 (s, 3H); mass spectrum m/e 374 (M^+).

Anal: Calcd for $C_{22}H_{18}N_2SO_2$: C, 70.57; H, 4.85; N, 7.48; S, 8.56. Found: C, 70.32; H, 4.70; N, 7.28; S, 8.20.

Preparation of Sodium Salts of Tosylhydrazones. The sodium salts of the tosylhydrazones were prepared in a nitrogen atmosphere dry box by dissolving the hydrazone in dry tetrahydrofuran (ca. 1 g/20 ml) and slowly adding with stirring one equivalent of sodium hydride (50% in mineral oil). The reaction was stirred for an additional hour after which a three-fold volume of dry spectro-grade pentane was added to precipitate the salt. The salt was collected by filtration, washed with additional pentane and dried under vacuum. Although by weight the reaction was not always quantitative it was presumed to be analytically pure and subsequent reaction yields were based on amount of salt consumed

less any tosylhydrazone recovered.

Pyrolysis of 2-Ethynylbiphenyl-2'-Carboxaldehyde Tosylhydrazone Sodium Salt (33) in Benzene. A 3 oz Fisher-Porter Aerosol Compatibility Tube containing a magnetic stirring bar was charged with 2-ethynylbiphenyl-2'-carboxaldehyde tosylhydrazone sodium salt (33) (0.177 g, 0.45 mmol) and 40 ml of dry benzene under a nitrogen atmosphere. The tube was sealed and immersed into a pre-heated silicone oil bath at 125°C for 1.5 hr. After cooling the sodium p-toluenesulfinate was filtered and the benzene was removed on a rotary evaporator. The white crystals which remained were washed with ether (3 x 5 ml) to separate 9-(2,4,6-cycloheptatrien-1-yl)-phenanthrene (36) (an oil-soluble in ether) from 2H-phenanthro[9,10-c]pyrazole (37) (a solid, insoluble in ether). The ether washings were concentrated. Analysis by nmr and careful TLC with authentic material showed 9-(2,4,6-cycloheptatrien-1-yl)-phenanthrene (36) was not present. The pryrazole was isolated after vacuum drying in nearly quantitative yield and identical with that reported by Reimlinger[33] mp 275-278°C. Lit.[34] 282-283°C. Ir (KBr): 3400 (w), 3200-2800, 1612, 1578, 1545, 1450 (d), 1378, 1300-1000 (many weak bands), 955, 857, 755, 725, 614, 532 cm^{-1}; pmr (DMSO-d_6), δ8.0 (m, 5H), 6.5 (m, 5H); uv (CH_3CN): λ(ε): 340 (1075), 329 (1240), 324 (1222), 316 (1140), 285 (sh) (15,180), 267 (sh) (23,700), 250 (122,900), 244 (91,900), 220 nm (sh)

(33,800); mass spectrum m/e 218 (M^+), 190 (M^+-N_2).

Anal: Calcd. for $C_{15}H_{10}N_2$: C, 82.55; H, 4.64; N, 12.83. Found: C, 82.35; H, 4.58; H, 12.55.

Photolysis of Tosylhydrazone Sodium Salts of Aldehydes and Ketones. All photolyses were performed in the photolysis apparatus designed in these laboratories. It consisted of a large volume cooling jacket (11 cm diameter x 30 cm length, slivered on three sides) which contained an immersion well for the lamp and a #40 Pyrex O-ring ball joint (Figure 1). The sample was irradiated and cooled by placement in a long tube secured by the ball joint. Provision was made in this photolysis reaction tube for: a nitrogen atmosphere, solid additions, mechanical stirring, condensation of gases and thermocouple measurement of temperature. Sample was approxiamately 2 cm from lamp. In all cases a 550 W Hanovia "High-Pressure Quartz Mercury-Vapor Lamp" was employed. Temperature could be maintained anywhere from +20°C. to -120°C. by the circulating/ cooling system shown (Figure 2). Pentane, as the coolant, was circulated by a Cole-Palmer model 7004-62 magnetic drive centrifugal pump. Addition of controlled amounts of liquid nitrogen to the stainless steel Dewar flask (with copper coil submerged in pentane with high speed mechanical stirrer) afforded temperature regulation. The photolysis apparatus was immersed into a cold pentane filled Dewar also.

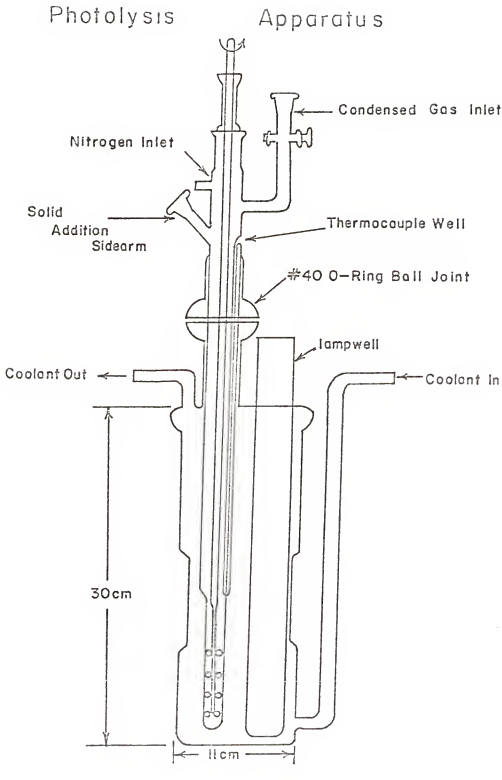

Photolysis Apparatus
Condensed Gas Inlet
Nitrogen Inlet
Solid
Addition
Sidearm
Thermocouple Well
#40 O-Ring Ball Joint
Lampwell
Coolant Out
Coolant In
30cm
11cm

Figure 1

Photolysis Cooling System

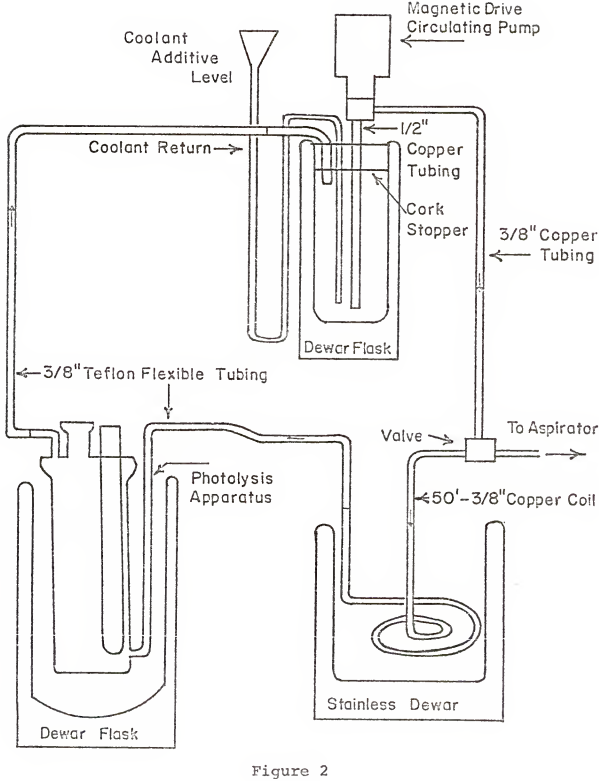


Figure 2

Photolysis of 9-Phenanthryl Carboxaldehyde Tosylhydrazone Sodium Salt (24') in Benzene/Tetrahydrofuran. To 20 ml of dry tetrahydrofuran and 10 ml of dry benzene in the photolysis reaction tube was added 0.237 g (0.598 mmol) of 9-phenanthryl carboxaldehyde tosylhydrazone sodium salt. This stirred suspension was photolyzed for 45 minutes at -60°C. After the reaction warmed to room temperature, the solvent was removed by rotary evaporator and the residue taken up in ether. This ether fraction was washed with water (2 x 50 ml) then saturated sodium sulfate solution (1 x 50 ml). After drying over anhydrous sodium sulfate the ether was evaporated and the residue separated by PTLC (elution with 80% pentane, 20% benzene). Only two compounds isolated were identified as shown in chart 1. The first was 9-(2,4,6-cycloheptatrien-1-yl) phenanthrene (36) and the second an inseparable mixture of 2-(9-phenanthrylmethyl)-oxolane (38) and 3-(9-phenanthrylmethyl)-oxolane (39) described as follows: Ir (neat, NaCl): 3290 (w), 3080-2880, 1601, 1595, 1500, 1450, 1430,1373, 1070, 955, 895, 797, 750, 729, 450 cm^{-1}; pmr ($CDCl_3$): δ8.6 (m, 2H), 7.6 (m, 7H), 4.4-3.3 (m, 5H), 1.8 (m, 4H); uv: (CH_3CN) λ(ε): 349 (397), 341 (305), 333 (512), 342 (sh) (440), 315 (sh) (660), 298 (10,900), 286 (10,250), 277 (13,000), 266 (sh) (16,000), 253 (53,662), 247 (sh) (46,500), 220 (32,477), 209 (45,167), 202 nm (44,250).

PHOTOLYSIS OF SODIUM SALTS AT VARIOUS TEMPERATURES

Sodium Salt	Solvent System	Temperature	Percent yields of		
			36	38+39	37
33	Benzene	30°C	6	--	60
	Benzene-THF (1:1)	-4°C	2	10	54
	Benzene-THF (1:2)	-70°C	8	12	42
24'	Benzene-THF (1:1)	-60°C	6	9	--

Chart 1

Anal. (on the mixture) calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92; Found: C, 86.72; H, 6.99.

Photolysis of 2-Ethynylbiphenyl-2'-Carboxaldehyde Tosylhydrazone Sodium Salt (33) in a Benzene/Tetrahydrofuran System at Various Temperatures. To approximately 30 ml of the appropriate solvent combination (see Chart 1) in the photolysis reactor tube was added an exact quantity of 2-ethynylbiphenyl-2'-carboxaldehyde tosylhydrazone sodium salt (33) (ca. 1/4 g) under nitrogen. The stirred suspension was photolyzed for 35 minutes and then allowed to warm to room temperature. Any precipitate was filtered and solvent removed on a rotary evaporator. To the residue was added 5 ml methylene chloride, filtered (to remove pyrazole), crystals washed with methylene chloride (2 x 1 ml), methylene chloride solutions combined and evaporated to dryness. PTLC was employed on the remaining yellow oil The major products were 9-(2,4,6-cycloheptatrien-1-yl)-phenanthrene (36) and an inseparable mixture of 2-(9-phenanthrylmethyl)-oxolane (38) and 3-(9-phenanthryl-methyl) oxolane (39).

Photolysis of 9-Phenanthryl Carboxaldehyde Tosylhydrazone Sodium Salt (24') in Dimethyl Ether. 9-Methoxymethyl Phenanthrene (40). Dimethyl ether (30 ml) was condensed into the photolysis reaction tube. 9-Phenanthryl carboxaldehyde tosylhydrazone sodium salt (24') (0.328 g, 0.828 mmol) was added and irradiated for 65 minutes at -60°C under nitrogen with stirring. The

reaction was allowed to warm to room temperature and the dimethyl ether to evaporate. The residue was taken up in methylene chloride (50 ml) and washed with water (3 x 50 ml) then saturated sodium sulfate solution (1 x 50 ml). After drying over anhydrous magnesium sulfate, the methylene chloride was removed on a rotary evaporator. The oil which remained was separated into its components by PTLC (elution with 75% pentane, 25% benzene). Although 0.144 g of 9-phenanthryl carboxaldehyde tosylhydrazone was recovered, the major product, in 40% yield was 9-methoxymethyl phenanthrene (40): bp 110°-120°C (0.25 mm); ir (neat, NaCl): 2930, 1610, 1490, 1315, 1190, 1102, 1089, 888, 748, 721 cm^{-1}; pmr ($CDCl_3$): δ8.6 (m, 2H), 7.6 (m, 7H), 4.90 (s, 2H), 3.45 (s, 3H); mass spectrum: m/e 222 (M^+), 205 ($M^+ - CH_5$) (Ar-C≡O$^+$), 193 ($M^+ - OCH_3$).

Anal: Calcd for $C_{16}H_{14}O$: C, 86.49; H, 6.31; Found: C, 86.24; H, 6.19

Photolysis of 2-Ethynylbiphenyl-2'-Carboxaldehyde Tosylhydrazone Sodium Salt (33) in Dimethyl Ether. Dimethyl ether (30 ml) was condensed into the photolysis reaction tube and 0.236 g (0.597 mmol) of 2-ethynylbiphenyl-2'-carboxaldehyde tosylhydrazone sodium salt (33) was added and irradiated for 1 hr under nitrogen at -110°C with stirring.

The salt (33) was slightly soluble in liquid dimethyl ether (ca. 1 mg/ml). However, normally a ratio of 250 mg/ 30 ml was used in photolysis and, thus,

mixtures of this sort were vigorously stirred while irradiating. After the reaction was completed a clear, pale yellow solution was usually observed (even the sodium p-toluenesulfinate was dissolved). The solution was allowed to warm to room temperature and the dimethyl ether to evaporate. The residue was taken up in methylene chloride (50 ml) and washed with water (3 x 50 ml) and then saturated sodium sulfate solution (1 x 50 ml). After drying over anhydrous magnesium sulfate the methylene chloride was evaporated on a rotary evaporator. Yellow crystals remained which were washed with three 10 ml protons of anhydrous ether to give 20 mg of white crystals of analytically pure 2H-phenanthro(9,10-c]pyrazole (37) (15%) (no depression in mixed melting point). The ether washings were combined and evaporated to a yellow oil. PTLC of the yellow oil (elution with 75% pentane, 25% ether, run concurrently with authentic sample) gave 11%, isolated yield, of 9-methoxymethyl phenanthrene (40) (confirmed by nmr).

Photolysis of 2H-Dibenzo[a,c]cyclohepten-5-one Tosylhydrazone Sodium Salt (41) in Dimethyl Ether. Dimethyl ether (30 ml) was condensed into the photolysis reaction tube and 0.203 g (0.512 mmol) of 2H-dibenzo-[a,c]cyclohepten-5-one tosylhydrazone sodium salt (41) was added and irradiated for 45 min under nitrogen at -110°C with stirring. The solution was allowed to warm to room temperature and the dimethyl ether to evaporate.

The residue was taken up in methylene chloride (50 ml) and washed with water (3 x 50 ml) and then saturated sodium sulfate solution (1 x 50 ml). After drying over anhydrous magnesium sulfate the methylene chloride was evaporated on a rotary evaporator to give approximately 100 mg of a yellow oil. PTLC of the oil (75% pentane, 25% ether, run concurrently with authentic 9-methoxymethyl phenanthrene (40)) gave no compound with identical R_f value as the latter. Analysis of bands with similar R_f value as the latter by nmr (but not identical) confirmed the total absence of 9-methoxymethyl phenanthrene. No attempt was made to identify any other material.

Photolysis of 2-Ethynylbiphenyl-2'-Carboxaldehyde Tosylhydrazone Sodium Salt (33) in Dimethyl Ether in the Presence of Triethyl Amine. Dimethyl ether (30 ml) was condensed into the photolysis reaction tube and 0.165 g (0.421 mmol) of 2-ethynylbiphenyl-2'-carboxaldehyde tosylhydrazone sodium salt (33) and 0.5 ml of triethyl amine were added. The suspension was stirred and irradiated under nitrogen at -110°C for 45 minutes. After warming to room temperature and allowing the solvent to evaporate, work-up as above gave 37 mg of 2H-phenanthro[9,10-c] pyrazole (37) (37%) and less than 2% of 9-methoxymethyl phenanthrene (40).

Photolysis of 5H-Dibenzo[a,c]cyclohepten-5-one Tosylhydrazone Sodium Salt (41) in 1,3-Butadiene. 1,3-Butadiene (30 ml) was condensed into the photolysis

reaction tube and 0.270 g (0.682 mmol) of 5H-dibenzo[a,c]cyclohepten-5-one tosylhydrazone sodium salt (41) was added and photolyzed for one hour at -65°C under nitrogen with stirring. The reaction was allowed to warm to room temperature and the butadiene to evaporate. The residue was taken up in methylene chloride (50 ml) and washed with water (3 x 50 ml) then saturated sodium sulfate solution (50 ml). After drying over anhydrous magnesium sulfate, the solvent was removed on a rotary evaporator. The residue was chromatographed by PTLC. The major product was 8b,8c,9,12-tetrahydrobenzo-[1,3] cyclopropa[1,2-l]phenanthrene (42) (0.045 g, 30% yield). Ir (neat, NaCl): 3068, 3028, 2925, 2855, 1600, 1445, 1295, 1260, 1005, 890, 785, 738 cm^{-1}; pmr ($CLCl_3$): δ8.1-7.0 (m, 8H), 5.62 (d, 2H), 2.55 (m, 5H), 0.7-0.4 (m, 1H); mass spectrum: Found: m/e 244.1247 (Calcd for $C_{19}H_{16}$: m/e 244.1251).

Photolysis of 2-Ethynylbiphenyl-2'-Carboxaldehyde Tosylhydrazone Sodium Salt (33) in Dimethyl Ether and 1,3-Butadiene. Dimethyl ether (20 ml) and 1,3-butadiene (15 ml) were condensed into the photolysis reaction tube and 0.243 g (0.613 mmol) of 2-ethynylbiphenyl-2'-carboxaldehyde toslhydrazone sodium salt (33) was added and irradiated for 1 hr under nitrogen at -110°C with stirring. The solution was then allowed to warm to room temperature and the solvents to evaporate. The residue was taken up in methylene chloride (50 ml) and washed

with water (3 x 50 ml) and then saturated sodium sulfate solution (1 x 50 ml). After drying over anhydrous magnesium sulfate, the methylene chloride was evaporated on a rotary evaporator. Ether (10 ml) was added to the yellow oily crystals which remained. The yellow ether solution was filtered and the off-white solid which remained in the filter was washed with 2 x 10 ml portions of ether. The white solid was vacuum dried and, by mixed melting point, was determined to be analytically pure 2H-phenanthro[9,10-c]pyrazole (37) (30% yield). The ether washings were combined and evaporated to give a yellow oil. The oil was separated into its components by PTLC (elution with 75% pentane, 25% ether, run concurrently with authentic samples) to give 5% of 8b,8c,9,12-tetrahydrobenzo[1,3]cyclopropa[1,2-l]phenanthrene (42) and 11% of 9-methoxymethyl phenanthrene (40) (confirmed by nmr): This experiment was repeated on two other occasions. The figures given were the average, isolated percent yields for three duplicate runs.

Photolysis of 2-Ethynylbiphenyl-2'-Carboxaldehyde Tosylhydrazone Sodium Salt (33) in Dimethyl Ether and 1,3-Butadiene in the Presence of Triethyl Amine. Dimethyl ether (20 ml) and 1,3-butadiene (15 ml) were condensed into the photolysis reaction tube. 2-Ethynylbiphenyl-2'-carboxaldehyde tosylhydrazone sodium salt (33) (0.243 g, 0.613 mmol) and triethyl amine (0.5 ml)

were added and were irradiated for one hour under nitrogen with stirring at -110°C. After allowing the reaction to warm to room temperature and the solvent to evaporate, work-up as above gave the following: 2H-phenanthro[9,10-c] pyrazole (37), 34%; 9-methoxymethyl phenanthrene (40), < 1%; 8b,8c,9,12-tetrahydrobenzo[1,3]cyclopropa[1,2-l] penanthrene (42), 4%. A duplicate run was carried out with these results: pyrazole (37), 56%; methyl ether (40), 0.5%; olefin (42), 4%.

Photolysis of 2-Ethynylbiphenyl-2'-Carboxaldehyde Tosylhydrazone Sodium Salt (33) in Cyclopentadiene. Cyclopentadiene (30 ml) was distilled from the dimer and added to the photolysis reaction tube. 2-Ethynyl-biphenyl-2'-carboxaldehyde tosylhydrazone sodium salt (33) (0.206 g, 0.513 mmol) was added and the stirred suspension was irradiated for 30 minutes under nitrogen at -60°C. After warming to room temperature the reaction mixture was evaporated to dryness on a rotary evaporator. To the residue 10 ml of ether were added and then subsequently filtered. The yellow residue in the filter was washed with ether, dried, and determined by mixed melting point to be analytically pure 2H-phenanthro[9,10-c]pyrazole (37), (55% yield). The ether washings were combined and evaporated. PTLC of the resulting oil gave a band which approximately corresponded to endo-2,3-(o-biphenylenyl)-tricyclo[3.2.1.$0^{2,4}$]-oct-6-ene (45). A uv spectrum of the material in this band, however, failed to agree

with the uv spectrum reported[32] for (45). Although it was obvious other compounds were present, they were not characterized or isolated.

Pyrolysis of 9-Phenanthryl Carboxaldehyde Tosylhydrazone Sodium Salt (24') in Benzene with Dimethyl Fumarate. A Fisher-Porter Compatibility tube was charged in a nitrogen atmosphere with 0.410 g (1.04 mmol) of 9-phenanthryl carboxaldehyde tosylhydrazone sodium salt (24'), 0.149 g (1.04 mmol) of dimethyl fumarate, 30 ml of dry benzene, and a magnetic stir bar. The tube was sealed and placed in a magnetically stirred, pre-heated oil bath at 125°C for 30 minutes. The tube was then cooled and the benzene was evaporated. The residue was taken up in methylene chloride (50 ml) and washed with water (3 x 50 ml) then with saturated sodium sulfate solution (1 x 50 ml). After drying over anhydrous magnesium sulfate, the solvent was removed on a rotary evaporator. The residue was placed in a large sublimator and heated at 50°C for 2 hrs (0.1 mm) to remove excess dimethyl fumarate. PTLC on the residue in the sublimator gave 0.096 g (26%) of a mixture of stereoisomers of 3,4-dicarbomethoxy-5-(9-phenanthryl)-2-pyrazoline (46) Mp 76-81°C (ethanol/water); ir (KBr): 3364 (broad), 3045, 2980, 2965, 2840, 1743, (sh), 1740, 1560, 1450, 1430, 1210, 1172, 1096, 1024, 749, 719, 674, 604, cm^{-1}; pmr ($CLCl_3$): δ8.5-8.2 (m, 2H), 8.0-7.3 (m, 7H), 6.9-6.4 (broad s, 1H), 4.85 (broad d, 1H), 3.95 (m, 1H), 3.83

(s, 3H), 3.77 (s, 3H); mass spectrum: Found: m/e 362.4321 (Calcd for $C_{21}H_{18}N_2O_4$: m/e 352.4347).

Photolysis of 9-Phenanthryl Carboxaldehyde Tosylhydrazone Sodium Salt in Dimethyl Ether in the Presence of Dimethyl Fumarate. Dimethyl ether (30 ml) was condensed into the photolysis reaction tube. 9-Phenanthryl carboxaldehyde tosylhydrazone sodium salt (0.228 g, 0.58 mmol) and dimethyl fumarate (1.526 g, 10.6 mmol) (soluble) was added. The suspension of the salt was stirred and irradiated for 1.5 hr at -100°C under nitrogen. The reaction was allowed to warm to room temperature and the dimethyl ether to evaporate. The residue was taken up in methylene chloride and after work-up as above, 9-phenanthryl carboxaldehyde was isolated, 52 mg, 43% yield. No compound was present in the preparative thick layer chromatograph that had an identical R_f value as the pyrazole (46). Bands that were within 0.1-0.2 R_f units (46) were examined by nmr and were found to bear no resemblance in any respect to that of the pyrazole.

Photolysis of 2-Ethynylbiphenyl-2'-Carboxaldehyde Tosylhydrazone Sodium Salt (33) in Dimethyl Ether in the Presence of Dimethyl Fumarate. Dimethyl ether (30 ml) was condensed into the photolysis reaction tube. 2-Ethynylbiphenyl-2'-carboxaldehyde tosylhydrazone sodium salt (33) (0.316 g, 0.797 mmol) and dimethyl fumarate (1.599 g, 11.1 mmol) were added and photolyzed as above

for one hour. The reaction was allowed to warm to room temperature and the solvent to evaporate. Methylene chloride (50 ml) was added to the residue and this was washed with water (3 x 50 ml) and then saturated sodium sulfate solution (1 x 50 ml). After drying over anhydrous magnesium sulfate, the solvent was removed on a rotary evaporator. The residue was placed in a large sublimator and heated at 50°C for 2 hr (0.1 mm) to remove excess dimethyl fumarate. After cooling 10 ml of ether was added to the residue in the sublimator. A precipitate formed which was filtered and washed twice with 10 ml portions of ether. The ether washings were combined and evaporate. PTLC on the residue (with authentic material for comparison) showed that there was not present any 3,4-dicarbomethoxy-5-(9-phenanthryl)-2-pyrazoline (46) or 9-phenanthryl carboxaldehyde. This was substantiated by nmr spectra on chromatographed materials.

2-[2'-(Phenylethynyl)-2-biphenylyl]-1,3-dioxolane (49). To a 100 ml dry three neck round bottom flask equipped with mechanical stirrer, nitrogen inlet and condenser was added 2-[2'-(ethynyl)-2-biphenylyl]-1,3-dioxolane (31) (0.535 g, 2.4 mmol), iodobenzene (0.436 g, 2.13 mmol), cuprous iodide* (0.200 g, 1.04 mmol), 15 ml dimethyl-

*It was found the nature of the cuprous iodide used in this reaction was very critical. Best results were obtained using a sample purchased from Ventron. Cuprous iodide from

formamide (dried over 4A sieves) and anhydrous potassium carbonate (0.1 g). The mixture was stirred vigorously and refluxed under nitrogen for three hours. After cooling to room temperature the black solution was poured into 200 ml water and extracted with methylene chloride (3 x 50 ml). Extracts were combined and evaporated on a rotary evaporator. The residue was dissolved in ether and washed with water (3 x 50 ml), saturated sodium sulfate solution (2 x 50 ml) and dried over anhydrous magnesium sulfate. After evaporation of the ether, 0.601 g of a dark oil was isolated which, despite its appearance, appeared to be quite pure as shown by nmr. The oil was chromatographed over silica gel eluting with 75% pentane, 25% ether. White crystals of 2-[2'-(phenylethynyl)-2-biphenylyl]-1,3-dioxolane (49) were isolated (.418 g, 60%) and could be recrystallized from ether/pentane at -78°C. Mp 120.5-122°C; ir (KBr): 3060, 2900, 1595, 1490, 1440, 1400, 1275, 1200, 1063, 964, 940, 750, 695, 639, 519; pmr ($CLCl_3$): δ7.4-7.0 (m, 13H), 5.65 (s, 1H), 3.9 (m, 4H); mass spectrum m/e 326 (M^+).

Anal: Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56; Found: C, 84.62; H, 5.57.

2-(Phenylethynyl)-Biphenyl-2'-Carboxaldehyde (50).

Matheson, Coleman and Bell gave less than 5% product. Cuprous iodide prepared in these laboratories by the method of Kauffman and Pinnell[69] resulted in the same disappointing yields.

2-[2'-(Phenylethynyl-2-biphenylyl]-1,3-dioxolane (49) could be hydrolyzed to the aldehyde in a manner analogous to 2-[2'-(ethynyl)-2-biphenylyl]-1,3-dioxolane (31) (vide infra). Work-up as usual gave a yellow oil which was chromatographed on silica gel, elution with 75% pentane, 25% ether. A very light yellow viscous oil resulted which if sublimed (130°C, 0.05 mm) deposited a solid white material on the dry-ice cooled cold finger but melted to an oil when warmed to room temperature. Ir (NaCl, neat): 3030, 2920, 1685, 1591, 1440, 1200, 750; pmr ($CLCl_3$) δ9.8 (s, 1H), 7.4-7.0 (m, 13H).

2-(Phenylethynyl)-Biphenyl-2'-Carboxaldehyde Tosylhydrazone (51). To 0.517 g (1.85 mmol) of 2-(phenylethynyl)-biphenyl-2'-carboxaldehyde (50) in 5 ml of absolute ethanol in a round bottom flask equipped with a drying tube was added a solution of 0.344 g (1.85 mmol) of tosylhydrazide in 5 ml of absolute ethanol and 0.25 drop of concentrated sulfuric acid. The solution was stirred at room temperature for one day and then allowed to sit for two days at -15°C. The solution was then poured into water (100 ml) and extracted with methylene chloride (3 x 50 ml). The extracts were combined, dried over magnesium sulfate, concentrated on a rotary evaporator, and chromatographed over silica gel (elution with 50% pentane, 50% ether). After drying under vacuum, 0.65 g (75% yield) of a light yellow glass was obtained that could not be induced to crystalize. Ir (neat, NaCl):

3090, 3030, 1605, 1490, 1430, 1360, 1320, 1165, 1045 945, 820, 740, 652 cm^{-1}; pmr ($CLCl_3$): δ8.1-7.0 (m, 19H), 3.34 (s, 3H).

Anal: Calcd for $C_{28}H_{22}N_2SO_2$: C, 74.65; H, 4.92; N, 6.22; S, 7.11. Found: C, 74.48; H, 4.96; H, 6.13 S, 7.21.

9-Bromophenanthrene (53). Phenanthrene was brominated according to the procedure of May and Mosettig.[40] The crude product was distilled at 157°C at 0.75 mm. 9-Bromophenanthrene was isolated in 85% yield and recrystalized from petroleum ether. mp 59-60°C. Lit.[40] 61.5-63°C.

9-Cyanophenanthrene (54). Following the procedure of Goldberg, Ordas and Carsch,[41] 9-cyanophenanthrene (54) was prepared in 80% yield from the above 9-bromophenanthrene (53). Bp 200-220°C (2-4 mm); mp 105-107°C. Lit.[41] mp 104.5-.06°C.

9-Benzoyl Phenanthrene (55). Phenyl magnesium bromide was added to 9-cyanophenanthrene (54) according to the method of Fuson and Strycker.[42] After acid hydrolysis, a 75% yield of 9-benzoyl phenanthrene was obtained. Mp 89-90°C Lit.[42] mp 90-91°C.

9-Benzoyl Phenanthrene Tosylhydrazone (56). To a 100 ml round bottom flask with condenser and drying tube was added 9-benzoyl phenanthrene (55) (2.00 g, 7.1 mmol) and 0.5 ml concentrated sulfuric acid. The solution was heated to reflux and tosylhydrazide (1.35 g,

7.2 mmol) added. Heating was continued for 14 hours after which crystals had formed. The reaction was cooled, crystals collected and washed with cold ethanol. White crystals of 9-benzoyl phenanthrene tosylhydrazone (56) were obtained, 1.70 g (53%). Recrystalization was from toluene. mp 209-210°C. Ir (KBr): 3158, 1578, 1479, 1434, 1372, 1330, 1155, 1071, 1028, 1004, 948, 881, 869, 822, 802, 738, 710, 654 , 581, 531 cm^{-1}; pmr ($CLCl_3$): δ8.6 (d, 2H), 7.8-7.1 (m, 15H), 2.43 (s, 3H); ms: 450 (molecular ion), 295 ($M^+-SO_2C_6H_4CH_3$).

Anal: Calcd. for $C_{28}H_{22}N_2SO_2$: C, 74.65; H, 4.92. Found: C, 74.59; H, 4.97.

Pyrolysis of 9-Benzoyl Phenanthrene Tosylhydrazone Sodium Salt (57) in Benzene. A Fisher-Porter Compatibility Tube was charged in a dry box with 0.300 g (0.641 mmol) of 9-benzoyl phenanthrene tosylhydrazone sodium salt (57), 30 ml of dry benzene, and a magnetic stir bar. The tube was sealed and immersed into a magnetically stirred, pre-heated oil bath at 125°C for 30 minutes. After cooling the benzene was evaporated on a rotary evaporator. The residue was taken up in methylene chloride (50 ml) and washed with water (3 x 50 ml) and then saturated sodium sulfate solution (1 x 50 ml). After drying over anhydrous magnesium sulfate, the methylene chloride was removed by a rotary evaporator. The yellow glass which remained was separated into two components by PTLC (elution with 75% pentane, 25% ether). The first was

identified as 4-(9-phenanthryl)-3-phenyl-1,3,5-cycloheptatriene (58): 22% yield; mp 192-195°C (ethanol/water); ir (KBr): 3020, 1595, 1475, 1445, 1433, 1068, 1035, 945, 905, 943, 745, 724, 700, 605, 585, 510, 429 cm^{-1}; mpr ($CLCl_3$): δ8.6 (m, 2H), 7.7-6.8 (m, 12H), 6.2-6.0 (m, 2H), 5.7-5.4 (m, 2H), 3.1 (t, 2H); mass spectrum: Found: m/e 344.1581 (Calcd for $C_{27}H_{20}$: m/e 344.1565).

The second was identified as 9-benzoyl phenanthrene azine (60): mp 180-5°C (ethanol/water); 55% yield; ir (KBr): 3030, 1590, 1560, 1492, 1441, 1321, 1262, 891, 746, 722, 690, 610 cm^{-1}; pmr ($CLCl_3$): δ8.7 (m, 4H), 7.8-6.9 (m, 24H); mass spectrum: Found: m/e 560.2223 (Calcd for $C_{42}H_{28}N_2$: m/e 560.2251).

Pyrolysis of 2-(Phenylethynyl)-Biphenyl-2'-Carboxaldehyde Tosylhydrazone Sodium Salt (52) in Benzene. A Fisher-Porter Compatibility Tube was charged in a nitrogen dry box with 50 mg of 2-(phenylethynyl)-biphenyl-2'-carboxaldehyde tosylhydrazone sodium salt (53), 30 ml of dry benzene, and a magnetic stir bar. The tube was sealed and immersed into a magnetically stirred,pre-heated oil bath at 125°C for 30 minutes. After cooling the benzene was evaporated on a rotary evaporator. The residue was taken up in methylene chloride (50 ml) and washed with water (3 x 50 ml) and then saturated sodium sulfate solution (1 x 50 ml). After drying over anhydrous magnesium sulfate, the methylene chloride was evaporated by a rotary evaporator. Nearly white crystals remained. These were washed with anhydrous ether (3 x 10 ml) and

vacuum dried. Thirty-four milligrams of a white solid was obtained (94% yield) identical with that reported by Van Alphen[44] for 3-phenyl-2H-phenanthro[9,10-c]pyrazole(61). Mp: 252-253°C. Lit.[44] 245°C (from methanol with trace of hydroxide).

The ether washings were combined and concentrated. TLC, PTLC (concurrently with authentic material), and nmr could not detect any 4-(9-phenanthryl)-3-phenyl-1,3,5-cycloheptatriene (58).

Photolysis of 2-(Phenylethynyl)-Biphenyl-2'-Carboxaldehyde Tosylhydrazone Sodium Salt (52) in Benzene. Benzene (30 ml) and 2-(phenylethynyl)-biphenyl-2'-carboxaldehyde tosylhydrazone sodium salt (52) (50 ml, 0.106 mmol) were added to the photolysis reaction tube. The stirred suspension was photolyzed for 30 minutes under nitrogen at 10°C. After warming to room temperature, work-up as above gave 24 mg of 3-phenyl-2H-phenanthro (9,10-c]pyrazole (75%) and 2 mg of 4-(9-phenanthryl)-3-phenyl-1,3,5-cycloheptatriene (58) (5.5%).

Photolysis of 9-Benzoyl Phenanthrene Tosylhydrazone Sodium Salt (56) in Dimethyl Ether and 1,3-Butadiene. Dimethyl ether (20 ml) and 1,3-butadiene (15 ml) were condensed into the photolysis reaction tube. 9-Benzoyl phenanthrene tosylhydrazone sodium salt (56) (0.438 g, 0.834 mmol) was added and the stirred suspension was photolyzed for one hour under nitrogen at -110°C. After warming to room temperature and allowing the solvents

to evaporate, the residue was taken up in methylene chloride and washed with water (3 x 50 ml) and then saturated sodium sulfate solution (1 x 50 ml). The methylene chloride was removed on a rotary evaporator after being dried over anhydrous magnesium sulfate. The residue which remained was subjected to PTLC (elution 95% pentane, 5% ether); two products were isolated. The first was identified as a mixture of isomers of 1-(9-phenanthryl)-1-phenyl-2-vinyl cyclopropane (62) (59%): Ir (neat, NaCl); 3040, 3010, 1949, 1797, 1635, 1600, 1493, 1450, 1035, 990, 943, 900, 751, 724, 702 cm^{-1}; pmr ($CDCl_3$): δ8.7-8.3 (m, 2H), 8.0-6.9 (m, 12H), 5.34-4.75 (m, 3H), 2.8-2.2 (broad m, 1H), 2.0-1.2 (m, 2H). Mass spectrum: Found: m/e 320.4444 (Calcd for $C_{25}H_{20}$: m/e 320.4443).

The second was identified as 9-(methoxyphenylmethyl)-phenanthrene (63) (7%): Ir (neat, NaCl): 3035, 2961, 2912, 1950, 1722, 1600, 1491, 1450, 1312, 1248, 1187, 1092, 1031, 970, 900, 750, 725, 700 cm^{-1}; pmr ($CDCl_3$): δ8.8-8.6 (m, 2H), 8.1-7.1 (m, 12H), 5.86 (s, 1H), 3.47 (s, 3H): mass spectrum: Found: m/e 298.2222 (Calcd for $C_{22}H_{18}O$: m/e 298.2223).

Photolysis of 2-(Phenylethynyl)-Biphenyl-2'-Carboxaldehyde Tosylhydrazone Sodium Salt (52) in Dimethyl Ether and 1,3-Butadiene. Dimethyl ether (20 ml) and 1,3-butadiene (15 ml) were condensed into the photolysis reaction tube. 2-(Phenylethynyl)-biphenyl-2'-carbox-

aldehyde tosylhydrazone sodium salt (52) (0.133 g, 0.281 mmol) was added and irradiated for one hour under nitrogen with stirring at -110°C. After warming to room temperature and allowing the dimethyl ether and butadiene to evaporate, the residue was taken up in methylene chloride (50 ml) and washed with water (3 x 50 ml) and then saturated sodium sulfate solution (1 x 50 ml). After drying over anhydrous magnesium sulfate, the methylene chloride was evaporated on a rotary evaporator. To the yellow residue was added 10 ml of anhydrous ether. The white precipitate which formed was filtered and washed with two 10 ml portions of ether. The white crystals which remained were determined by mixed melting point (no depression) to be pure 3-phenyl-2H-phenanthro[9,10-c]pyrazole (61) (48%). The ether washing were combined, concentrated and subjected to PTLC (elution with 95% pentane, 5% ether, run concurrently with authentic materials). All products were scrutinized by nmr. Only 1-(9-phenanthryl)-1-phenyl-2-vinyl cyclopropane (62) (6.7%) and 9-(methoxyphenylmethyl)-phenanthrene (63) (1%) could be identified. All other material appeared to be either dimeric or polymeric aromatic hydrocarbon.

Photolysis of 2-(Phenylethynyl)-Biphenyl-2'-Carboxaldehyde Tosylhydrazone Sodium Salt (52) in Dimethyl Ether and 1,3-Butadiene in the Presence of Triethyl Amine. Dimethyl ether (20 ml) and 1,3-Butadiene (15 ml) were condensed into the photolysis reaction tube.

2-(Phenylethynyl)-biphenyl-2'-carboxaldehyde tosylhydrazone sodium salt (52) (50 mg, 0.106 mmol) and triethyl amine (0.2 ml) were added and the stirred suspension was irradiated for 30 minutes under nitrogen at -110°C. After work-up as above the following product yields were realized: 3-phenyl-2H-phenanthro[9,10-c]pyrazole (61), 9.4%; 9-(methoxyphenylmethyl)-phenanthrene (63), 1.5%.

2-(Phenylethynyl)-biphenyl-2'-Carboxaldehyde Oxime (64). To a 20 ml round bottom flask with magnetic stirrer and condenser was added 2-(phenylethynyl)-biphenyl-2'-carboxaldehyde (50) (2.210 g, 7.83 mmol), hydroxylamine hydrochloride (0.837 g, 11.76 mmol), 10 ml pyridine and 10 ml ethanol. The solution was then refluxed for two hours, cooled to room temperature, poured into 3% hydrochloric acid and extracted with ether (3 x 100 ml). The ether extracts were dried with anhydrous sodium sulfate and then evaporated on a rotary evaporator to give 2.2 g of a yellow glass. Ir (neat, NaCl): 3000, 2900, 1580, 1480, 1425, 1300, 1200, 1064, 1030, 1004, 968, 869, 758, 701, 689 cm^{-1}. All of this material was used directly in the following.

2-(Phenylethynyl)-Biphenyl-2'-Carbonitrile (65). In a manner analogous to the method of Albright and Alexander,[46] to all of the above oxime was added 20 ml of dimethylformamide (dried over 4A siever), 2 ml of triethylamine and 5 ml of methyl isocyanate in a 50 ml round bottom equipped with a magnetic stirrer, condenser

and drying tube (Drierite^{R}). The solution was stirred at room temperature for 30 minutes and then heated at 110°C for 30 minutes more. The solution was then refluxed for an additional 30 minutes. After cooling to room temperature the solution was poured into water and extracted with ether (3 x 100 ml). The ethereal solution was washed with saturated sodium sulfate solution (3 x 100 ml) and dried over anhydrous magnesium sulfate. After evaporation of the ether on a rotary evaporator, there remained 2.370 g of a yellow/brown oil which was chromatographed over silica gel eluting with 95% pentane, 5% ether. 2-(Phenylethynyl)-biphenyl-2'-carbonitrile (65) (1.917 g) was isolated as a light yellow viscous oil. Yield: 92% (based on aldehyde). Ir (neat, NaCl): 3060, 2213, 1600, 1500, 1490, 1470, 1448, 1165 (w), 1119 (w), 1078 (w), 1009 (w), 962 (w), 923 (w), 758, 692 cm^{-1}. pmr ($CDCl_3$) δ7.65-7.4 (m), 7.4-7.2 (m), 7.1 (s); mass spectrum: Found: m/e 279.1042 (Calcd for $C_{21}H_{13}N$: m/e 279.1047).

Reduction of 2-(Phenylethynyl)-Biphenyl-2'-Carbonitrile (65) to 2-(Phenylethynyl)-Biphenyl-2'-Carboxaldehyde (50). To 0.705 g (2.52 mmol) of 2-(phenylethynyl)-biphenyl-2'-carbonitrile (65) in 20 ml absolute ethyl ether at -78°C under nitrogen was added slowly and with stirring 23 ml of a lithium aluminum hydride solution in ether (1 mg/ml, 0.63 mmol, 0.25 equiv). The reaction was stirred and let warm to room temperature overnight. The

reaction was then refluxed for 24 hr after which time an additional 23 ml of the same lithium aluminum hydride solution was added. The reflux was continued for 2 hr and then cooled to room temperature. Water (5 ml) was added cautiously followed by 25 ml of 5 M sulfuric acid. The ether solution was removed and the aqueous layer extracted with methylene chloride (3 x 50 ml). The organic extracts were combined and washed successively with 5% sodium bicarbonate solution (2 x 50 ml), water (2 x 50 ml), and saturated sodium sulfate (1 x 50 ml). The organic solution was dried over anhydrous sodium sulfate and then concentrated on a rotary evaporator. A yellow oil (0.517 g, 73% yield) was obtained after chromatography over silica gel (elution with 90% pentane, 10% ether) that was identical in all respects with 2-(phenylethynyl)-biphenyl-2'-carboxaldehyde (50) previously prepared.

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BIOGRAPHICAL SKETCH

John Peter Mykytka was born on July 30, 1946 in Coral Gables, Florida. He graduated from Christopher Columbus High School, Miami, Florida in 1964 and in 1968 received a Bachelor of Science in Chemistry from Loyola University, New Orleans, La. In September 1968, he enrolled in the University of Florida graduate school where he held both teaching and research assistanships.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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